

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM

PROCEEDINGS

VOLUME XXIX

Nº. 4

President: Prof. F. A. F. C. WENT

Secretary: Prof. L. BOLK

(Translated from: "Verslag van de gewone vergaderingen der Afdeeling
Natuurkunde", Vols. XXXIV and XXXV)

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Chemistry. — "*The Stability of Suspensoids under Influence of Electrolyte Mixtures.*" By Prof. H. R. KRUYT and P. C. VAN DER WILLIGEN.

(Communicated at the meeting of December 19, 1925).

On the influence of electrolyte mixtures on the limiting value of colloids there already exists an old investigation by LINDER and PICTON¹⁾ and another by FREUNDLICH and PAPE²⁾. Nevertheless it is only of late years that more attention has been devoted to this problem, in the hope of finding an explanation for the so-called ion-antagonisms, which play an important part in the biological sciences. It is particularly FREUNDLICH and SCHOLZ³⁾, WEISER⁴⁾, MUKHERJEE⁵⁾, GHOSH and DHAR⁶⁾, and SEN⁷⁾ who have occupied themselves with this problem. All these authors have especially tried to find an explanation of the phenomena found by them from considerations derived from the theory of adsorption. The differences in ion adsorption would govern the electrical phenomena and these again the conditions of stability in the colloids. It seems, however, preferable to us, to make direct investigations on the connection between the influence of electrolytes on the electric charge and that on the stability, leaving the cause of the change in the electric charge for the present an open question.

For some years researches have been going on in this laboratory on the influence of *two* electrolytes, which simultaneously make their influence felt on capillary-electric phenomena. From this point of view we examined both the potentials of flow in glass and cataphoretic phenomena of oil-emulsions. In due time we hope to publish a detailed account of these investigations, which have already been partly concluded. In this communication we only wish to draw attention to some researches on the limiting value of electrolyte mixtures in suspensoid sols, while in some cases at the same time the cataphoresis of these sols has been measured.

FREUNDLICH and PAPE's researches have shown that in the As_2S_3 sol the limiting values for potassium and sodium were perfectly additive, whereas in electrolytes which had cations of different charge or adsorbability,

1) Journ. Chem. Soc. 67, 67 (1895).

2) Z. Physik. Chem. 86, 458 (1914).

3) Koll. Beih. 14, 267 (1922).

4) Journ. Phys. Chem. 25, 665 (1921) and 28, 232 (1924).

5) Journ. Indian Chem. Soc. 1, 213 (1924).

6) Journ. Phys. Chem. 29, 435 and 659 (1925).

7) Z. Anorg. Chem. 149, 139 (1925). Journ. Phys. Chem. 29, 517 (1925).

the limiting values lay on the whole below the additive value. FREUNDLICH and SCHOLZ (loc. cit.) have found on the other hand that in the same sol Li and Mg exert such an influence that the joint value is situated above that of the components; in a certain sense the term of antagonism might be applied here. In his *Kapillarchemie*¹⁾ FREUNDLICH suggests a connection between the hydration of these sols and the said phenomenon.

In this investigation we have started from the assumption that every electrolyte which increases the charge, must necessarily increase the limiting value of a second electrolyte. For, the higher the charge, the further we are from the critical potential and the more of this second electrolyte must be added to reach the latter. Increase of the electric charge is in general to be expected in negatively charged colloids, when a salt is added with an anion that is polyvalent or strongly adsorbable. Thus ELLIS²⁾ found that the OH-ion increased the charge of oil-emulsions, POWIS³⁾, that the same might be said of $K_4Fe(CN)_6$, KRUYT and VAN ARKEL⁴⁾ finding a similar influence of the OH-ion in Se-sols. Finally one of us has found that the charging of a glass-capillary by added salts is a pretty general phenomenon⁵⁾, the result of which was recently confirmed by FREUNDLICH and ETTISCH⁶⁾.

We have now examined the limiting value of different sols. The results for the As_2S_3 -sol, the HgS-sol, and the Se-sol are recorded in the subjoined tables. In every column in these tables the quantity of salt is indicated as percentage of the limiting value of this salt in case the other is not present; between brackets this quantity is given in millimols per litre.

The experiments were carried out as follows: 10 cc. of sol were shaken, while 1 cc. of the first electrolyte was added, then 5 cc. of the second electrolyte in varying concentration; the total volume in the coagulation glass was, therefore, always 16 cc. The result was examined after a night's standing (16 hours).

When the addition of the two electrolytes took place at the same time, the same results were obtained.

The results of table 1 corroborate those of earlier investigators. It is seen that the addition of LiCl to the As_2S_3 -sol requires more $MgCl_2$ than in the pure sol. This is, therefore, the phenomenon to which the name of *antagonistic* action is given.

The same result is shown by tables 2 and 3 for the HgS-sol, and also by tables 4 and 5 though less pronounced. It appears, therefore, very clearly here that polyvalent anions have a stabilizing influence on the action. In a very peculiar way this finds also expression as follows:

1) H. FREUNDLICH, *Kapillarchemie* (Leipzig 1922), p. 635.

2) Z. Physik. Chem. **80**, 597 (1912).

3) Z. Physik. Chem. **89**, 91 (1915).

4) Rec. Trav. Chim. **40**, 170 (1921).

5) H. R. KRUYT, These Proc. **17**, 615 (1914); **19**, 1021 (1917); Koll. Z. **22**, 81 (1918).

6) Z. Physik. Chem. **116**, 401 (1925).

TABLE 1.
As₂S₃-sol

Li Cl	Mg Cl ₂
0 (0)	100 (0.8)
25 (24)	138 (1.1)
50 (48)	156 (1.25)
72 (69)	180 (1.45)
100 (96)	0 (0)

TABLE 2.
HgS-sol

$\frac{K_4 Fe(CN)_6}{4}$	Mg Cl ₂
0 (0)	100 (1.0)
12.5 (10)	180 (1.8)
20 (15)	190 (1.9)
25 (20)	200 (2.0)
44 (35)	230 (2.3)
62 (50)	60 (0.6)
100 (80)	0 (0)

TABLE 3.
HgS-sol

$\frac{K_3 Fe(CN)_6}{3}$	Mg Cl ₂
0 (0)	100 (1.0)
33 (10)	130 (1.3)
66 (20)	60 (0.6)
100 (30)	0 (0)

TABLE 4.
HgS-sol

$\frac{K_2 SO_4}{2}$	Mg Cl ₂
0 (0)	100 (1.0)
16 (5)	110 (1.1)
33 (10)	120 (1.2)
100 (30)	0 (0)

TABLE 5.
HgS-sol

K Cl	Mg Cl ₂
0 (0)	100 (1.0)
16 (5)	110 (1.1)
33 (10)	120 (1.2)
100 (30)	0 (0)

If a HgS-sol is left standing for some days, it sinks down, and soon the sol cannot be restored through shaking. If, however, 10 m. mol. of K₄Fe(CN)₆ have been added, the sol can be restored simply by shaking even after a month.

In table 6 measurements are recorded of the cataphoretic velocity of the HgS-sol by means of the apparatus of BURTON. It is seen from fig. 1 how well these measurements agree with the results of the preceding tables. In fact the ferro cyanide of potassium gives a large increase of the charge, KCl a small increase corresponding to the nature of the antagonistic actions found. MgCl₂ immediately decreases the charge.

In the tables 7, 8, 9, and 10 coagulation values are given for the selenium sol. Here antagonism is again clearly seen with the ferro cyanide of potassium, the effect is weaker with K₂SO₄, and fails to appear with KCl, just as with potassium acetate, the same thing being found for sodium picrate and benzoate.

It was known to us from the investigations of KRUYT and VAN ARKEL that KOH increases the charge of the selenium sol. To our astonishment table 11 showed us that nevertheless this substance did not raise the limiting

TABLE 6.
Cataphoretic velocity of the HgS-sol in the same dilution as in the
flaking experiments.
The velocity ν in microns per Volt per second.

Concentration	Cataphoretic velocity
sol + 10 m.mol $\frac{K_4 Fe(CN)_6}{4}$	3.5 μ
sol + 20 " "	3.8 μ
sol + 35 " "	3.2 μ
sol + 50 " "	2.2 μ
sol + 5 m.mol KCl	3.2 μ
sol + 10 " "	3.2 μ
sol + 20 " "	2.2 μ
sol + 0.6 m.mol $Mg Cl_2$	1.2 μ

value of $MgCl_2$. Quite conformable to the expectation, however, table 12 does yield the expected effect for the combination KOH and $BaCl_2$.

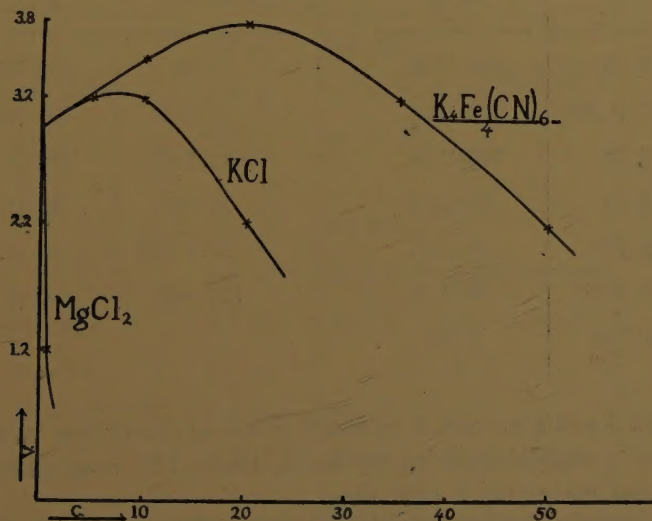


Fig. 1.

In table 13 we finally give measurements of the cataphoretic velocity in this sol; the measurements have been made according to the ultra-microscopic method of KRUYT and VAN ARKEL. Again, quite in accordance with what precedes, there appears to be increase of the charge in the case of potassium ferro cyanide and KOH.

We cannot satisfactorily account for the deviating behaviour of MgCl_2 . Something remarkable strikes us, however, in table 11, viz. that KOH in the smaller concentration does not change the limiting value of MgCl_2 , but

TABLE 7.
Se-sol

$\frac{\text{K}_4 \text{Fe}(\text{CN})_6}{4}$	Mg Cl_2
0 (0)	100 (3.0)
8 (5)	112 (3.4)
16 (10)	116 (3.5)
25 (15)	122 (3.7)
33 (20)	122 (3.7)
50 (30)	100 (3.0)
100 (60)	0 (0)

TABLE 8.
Se-sol

$\frac{\text{K}_2 \text{SO}_4}{2}$	Mg Cl_2
0 (0)	100 (3.0)
7.5 (3)	100 (3.0)
15 (5)	103 (3.1)
100 (40)	0 (0)

TABLE 9.
Se-sol

K Cl	Mg Cl_2
0 (0)	100 (3.0)
3 (1.25)	100 (3.0)
5 (2)	100 (3.0)
13 (5)	97 (2.9)
26 (10)	90 (2.7)
53 (20)	60 (1.8)
100 (38)	0 (0)

TABLE 10.
Se-sol

K acetaat	Mg Cl_2
0 (0)	100 (3.0)
6 (2.5)	100 (3.0)
12.5 (5)	100 (3.0)
25 (10)	80 (2.5)
37.5 (15)	66 (2.0)
100 (40)	0 (0)

that between 3 and 5 m. mol. it causes it to fall to a very low value. As this phenomenon is entirely wanting for BaCl_2 (table 12), a specific behaviour of the Mg -ion must play a part here.

We have further extended our investigation over the sols of the precious metals. Already FREUNDLICH and SCHOLZ had found in the Au -sol that no antagonistic phenomena appear there. We can confirm this (also for Pt and Ag) save for a remark to be made presently about the potassium ferrocyanides, but we have also been struck by another very remarkable fact. It is generally supposed that the hydroxyl-ion increases the stability of negatively charged sols. This supposition is confirmed by a value given by

TABLE 11.
Se-sol

KOH	Mg Cl ₂
0 (0)	100 (3.0)
1.2 (1)	100 (3.0)
2.5 (2)	100 (3.0)
3.7 (3)	97 (2.9)
5 (4)	30 (0.9)
6 (5)	3 (0.1)
12.5 (10)	<0.3 (<0.01)
25 (20)	<0.3 (<0.01)
100 (80)	0 (0)

TABLE 12.
Se-sol

KOH	Ba Cl ₂
0 (0)	100 (2.1)
3.7 (3)	120 (2.5)
6 (5)	175 (3.7)
12.5' (10)	192 (4.0)
25 (20)	165 (3.5)
55 (45)	100 (2.1)
100 (80)	0 (0)

TABLE 13.

Cataphoretic velocity of the Se-sol in the same dilution as in the flaking-experiments.
Velocity v in microns per Volt per second.

Concentration	Cataphoretic velocity	Concentration	Cataphoretic velocity
sol only	5.6 μ	sol only	5.6 μ
sol + 3 m.mol KOH	5.9 μ	sol + 5 m. mol $\frac{K_4 Fe(CN)_6}{4}$	6.0 μ
sol + 5 " "	6.1 μ	sol + 10 " "	6.4 μ
sol only	5.6 μ	sol only	5.6 μ
sol + 2 m.mol KCl	5.5 μ	sol + 2.5 m. mol Na benzoate	5.5 μ
sol + 5 " "	5.4 μ	sol + 5 " "	5.4 μ
sol + 10 " "	5.1 μ	sol only	5.6 μ
sol + 20 " "	4.7 μ	sol + 1.2 m. mol BaCl ₂	3.0 μ

FREUNDLICH ¹⁾ for the platinum sol, the limiting value of which for Na OH would be 130 m. mol, whereas that for NaCl is only $2\frac{1}{2}$. Remarkably enough the corresponding value for the gold-sol is not to be found in the literature. To our astonishment we found as limiting value observed after 16 hours 26 m. mol. for KCl, 20 m. mol. for KOH in a gold-sol prepared by electric dispersion. In a silver-sol, prepared likewise by dispersion, which

¹⁾ Z. Physik. Chem. 44, 152 (1903).

happened to give the same limiting value of 26 m.mol. for KCl, we also found again 20 m. mol. for KOH, while a repetition on the platinum-sol makes us doubt somewhat whether a value as we have described just now, may

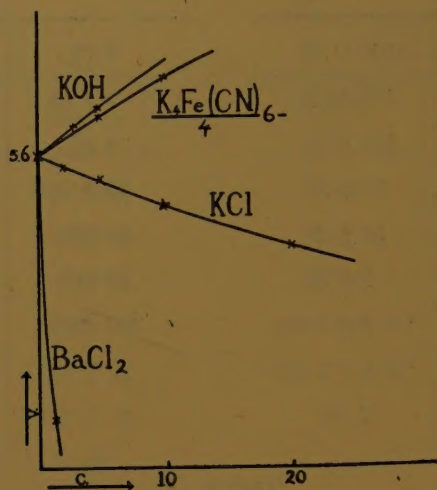


Fig. 2.

after all be assigned to FREUNDLICH's value for this sol. The limiting value which is found, depends in general somewhat on the interval that elapses between the addition of the electrolyte and the observation of the sol, but it now appeared that especially in the case of KOH this period is of the greatest influence. After one night's standing we found a limiting value of 140 m. mol., but when the estimation was made after two days' standing the flocculation concentration had shifted towards a value of about 20 m. mol., the limiting value for the neutral salts being by no means dependent on the time in the same degree.

Besides KOH appears not only to be inadequate to call forth antagonistic actions, but on the contrary it has a sensibilizing effect both on $MgCl_2$ and on $BaCl_2$. These experiences lead to the utter rejection of any supposition such as the charge of the sols of precious metals being attributed to absorbed hydroxyl ions. We get more the impression that the double layer in these sols is built up by complex compounds of the metals, and that alkaline surroundings have a very injurious influence on the structure of this double layer, at least that after a short time this double layer is destroyed ¹⁾.

Investigations with ferrocyanide and ferricyanide on these precious metal sols have shown us this: for the gold-sol every estimation is exceedingly difficult after five minutes, because the colour of these salt-solutions hampers the observation of the change of colour in a high degree, a chemical interaction between sol and electrolyte very soon setting in, in consequence of which a colourless solution remains. Nevertheless, on a rough examination

¹⁾ See WO. PAULI's papers of the last months in Koll. Beih. (Note added to the proofs).

of the colour, we got the impression that after all an antagonistic action of potassium ferro-cyanide and MgCl_2 does take place.

Summarizing we come to the conclusion that the cause of the so-called antagonistic flocculation effect is in general brought about by salts which increase the electric charge of the colloid. Undoubtedly polyvalence or good adsorbability of the ion of the same sign acts as a rule in this direction, but specific influences differing from sol to sol with respect to the same electrolyte make themselves felt here.

In connection with the investigations to which we alluded already above, we shall soon return to this subject.

VAN 'T HOFF-Laboratory.

Utrecht, December 1925.

Zoology. — "*On a new form of breathing regulation (regulation of diffusion) in Insects and Arachnida.*" By E. H. HAZELHOFF.
(Communicated by Prof. R. MAGNUS.)

(Communicated at the meeting of January 30, 1926).

Several investigators have described respiratory movements in a great number of Tracheata, corresponding in principal with those of Mammals and whereby an air-current is alternately drawn into and expelled from the respiratory organs.

Although it was expected, no trace of respiratory movements could be found in many Tracheata (Myriapoda, Arachnida, almost all Insect larvae and all pupae) even when highly magnified. WINTERSTEIN for instance says in his „Handbuch der vergleichenden Physiologie“, Band I, 2, pag. 111—112, that when one considers how exceptionally fine the extreme ramifications of the tracheal system are, one can hardly imagine how the tissues can receive a sufficient supply of oxygen. According to WINTERSTEIN this applies to both Tracheata with and without respiratory movements.

On page 113 WINTERSTEIN concludes: „Das Gesagte wird hinreichen, um zu zeigen, wie weit wir..... bei der Respiration der..... Insekten von einem Verständnis des Mechanismus ihres Gaswechsels in Wahrheit entfernt sind“.

A great improvement in this unsatisfactory state of the problem was caused by a short but very important paper by KROGH (A. KROGH. Studien über Tracheenrespiration II. Ueber Gasdiffusion in den Tracheen. Pflügers Archiv Band 179. 1920 pag. 95—112).

For a few Tracheata KROGH determines the normal amount of oxygen used. He then takes the average length and width of the tracheae and on the basis of these data he can now calculate, that an oxygen pressure difference of only a small percentage of one atmosphere is sufficient to cause inward diffusion of the required amount of oxygen.

In the Myriapod *Scutigera* e.g. an oxygen pressure head of 0.13 % of one atmosphere is sufficient (therefore an oxygen pressure of 20.93 %—0.13 % = 20.8 % in the extreme ramifications of the tracheal system); in the larva of *Cossus ligniperda* a diffusion head of 1.7 %; in the larva of *Tenebrio molitor* 2.2 %; and in the larva of *Lasiocampa* 1.7 %.

From these data the conclusion may be drawn that in many neither too large nor too active insects respiratory movements are absolutely superfluous as diffusion alone is quite sufficient to provide the tissues with oxygen. In very large and active Insects respiratory movements do occur.

It seems that former investigators have not realised sufficiently how

exceptionally short the distances are in which diffusion must take place, and that consequently the effect of diffusion has been underestimated.

In his calculations KROGH has not reckoned with the existence of tracheal valves near the stigmata. In the scarce and very scattered literature about the movements of these tracheal valves I found that these movements can be seen distinctly in several Orthoptera, owing to the fact that here the tracheal valves are joined to the stigmata. (In many other Insects the tracheal valves lie further from the stigmata so that their movements cannot be seen from the outside.)

In my investigations on *Periplaneta americana* it soon became evident that the first and second pairs of thoracic stigmata are mostly closed (or at least almost closed) when the insect does not move. Without hurting it, the insect was fastened to a corkplate by means of pins and placed in a trough closed hermetically with a cover of plate glass. An air-current (and afterwards also other gasmixtures) was drawn through the trough.

The fixing of the insect in a definite position is necessary as otherwise the stigmata are generally invisible.

Through a binocular microscope (magnification 10 or 20 times) the movements of the above named stigmata, especially those of the well developed first pair, are distinctly visible. The experiments were carried out at a constant temperature; usually at 28° C.

At a temperature of 28° C. *Periplaneta americana* shows no respiratory movements when at rest. The first two large thoracic stigmata mostly show very quick irregular oscillations (sometimes a few per second), whereby the opening of the stigmata generally remains very narrow, varying between 0 and $\frac{1}{10}$ or $\frac{1}{4}$ of the maximum opening¹⁾. When the insect moves the stigmata immediately open widely, and the quick oscillations cease. After the movements the stigmata still remain open for a short time (e.g. $\frac{1}{2}$ minute); then the quick oscillations of the stigmata reappear and the width of the opening gradually diminishes till it finally reaches its original state.

Apparently this must be considered as a peculiar form of breathing regulation, whereby the insect remains nearly passive. After an increase in the metabolism the intake of oxygen and output of carbon dioxide are increased by the enlargement of the stigmata (i. e. by improvement of the diffusion conditions), and not as could be expected by the appearance of real breathing movements. These movements do occur but only when the insect has been very active. The animal reacts on a lack of oxygen (respectively on too much of carbon dioxide) firstly by opening the stigmata and sometimes also by executing respiratory movements.

To determine exactly which stimulus causes the opening of the stigmata, I investigated the effect of different gas-mixtures, with a higher

¹⁾ At 12° C. the thoracic stigmata are closed or almost closed and the quick oscillations have ceased.

percentage of carbon dioxide or a lower percentage of oxygen than air.

It soon became evident that in a mixture with a low percentage of carbon dioxide (e.g. 2%) the stigmata open widely.

It was remarkable that a gas-mixture with only 10% oxygen (and 90 % nitrogen) never produced any effect; the insects were therefore not noticeably influenced by a considerable decrease of the oxygen pressure (a very low percentage of oxygen, e. g. 5 % and lower, really does cause the opening of the stigmata but at the same time also respiratory movements appear; a carbon dioxide pressure of 12 % or more produces the same effect).

We must therefore conclude, that the opening of the stigmata after the insect has moved is the result of the increased carbon dioxide pressure either in the tissues, or in the tracheae.

Furthermore I tried to determine if *Periplaneta* reacts on a increased carbon dioxide pressure in the tissues or on a increased carbon dioxide pressure in the neighbourhood of the stigmata.

A *Periplaneta* was fastened to a movable corkplate which was mounted in such a way, that with a slight movement the right or the left foremost thoracic stigma could be brought in the field of the binocular microscope. With the help of a fine glass capillary an air-current was directed towards the left stigma while from a second capillary a gas-current consisting of 5 % carbon dioxide and 95 % air was directed towards the right. Both stigmata apparently reacted quite independently of each other; the left stigma was closed or almost closed and the right wide open. When the 5 % carbon dioxide current on the right stigma was interrupted it closed after a short time (generally after one minute). When the 5 % CO₂ current was started again, the stigma reopened shortly afterwards (e. g. after 5 sec.; in one experiment the stigma reopened several times after 1 or 2 sec.). In these experiments the air-current was directed uninterruptedly towards the left stigma, and this stigma indeed remained closed or almost closed.

I now tried the effect of an interrupted air-current on the left stigma, while an uninterrupted 5 % carbon dioxide current was continuously flowing towards the right. The right stigma remained open, the left one opened $\frac{1}{2}$ to 2 minutes after the air-current was shut off and closed 1 to 5 sec. after the current was started again. Finally the same experiments were taken with the reversed, i. e. an air-current flowing towards the right stigma and a 5 % carbon dioxide current towards the left. The results quite agreed with what could be expected from the above.

All these results are satisfactorily explained if we suppose that the two foremost thoracic stigmata react absolutely independently of each other on the carbon dioxide pressure in their immediate neighbourhood. Apparently we are dealing with a peripheral regulation; from the very short reaction time it is obvious that the perception must take place near the stigma. In connection with this one is inclined to think of the sensory

hairs which were found by Alt (Zeitschrift für wissenschaftliche Zoologie; Band 99, 1912, pag. 378 en 379) on the thoracic stigmata of *Dytiscus marginalis*.

The phenomenon that stigmata, which are almost closed in the air, open in a gas-mixture with a low percentage of carbon dioxide, was furthermore observed in the book-lungs of three different Arachnida, namely: *Epeira diademata*, *Meta segmentata* and *Tetragnatha obtusa*. A peculiar difference between *Periplaneta* on the one hand and the three above mentioned Arachnida on the other hand is, that in Arachnida I never observed quick oscillations of the stigma. The experiments showed further, that in Arachnida a distinct *quantitative* relation exists between the carbon dioxide pressure of the surrounding air and the width of the stigma opening: in 1 % carbon dioxide the stigmata open slightly; in 1½, 2, 2½ and 4 % carbon dioxide they open more and more; in 5 % and especially in 8 or 10 % carbon dioxide the stigmata open very widely.

As in *Periplaneta* a decrease in the oxygen pressure to 10 % and even to 5 % of one atmosphere has no effect.

V. WILLEM (Observations sur la circulation sanguine et la respiration pulmonaire chez les Araignées. Arch. Néerl. de Physiol. de l'homme et des animaux. Tome I pag. 226. 1917) observed quick expansions and contractions of the complex of laminae of the book-lung of *Pholcus* synchronous with the beatings of the heart, and therefore in all probability caused by variations of the blood-pressure. The air-currents which, according to WILLEM, should be the result of these expansions and contractions, could however not be demonstrated (l.c. pag. 253).

On the basis of the quoted paper by KROGH and on the basis of my own investigations regarding the varying width of the stigma opening I think it probable that also in Arachnida diffusion is the most important process. One particular muscle which by its contraction causes a widening of the vestibulum of the book-lung, and which is considered by WILLEM as an inspiratory muscle, must, according to my opinion, be considered as the muscle which enlarges the width of the stigma opening in order to increase the speed of diffusion. I am of this opinion, because we see that at a low percentage of carbon dioxide this muscle does not contract repeatedly but only once, the stigma remaining open.

Further investigations regarding these problems are in course of preparation.

From the above it follows that the foremost thoracic stigmata of *Periplaneta* and also the stigmata of the book-lungs of different Arachnida are generally almost closed when the animal is at rest; a definite stimulus (a low percentage of carbon dioxide) is necessary to open them.

It is evident that when the stigmata are closed the conditions of diffusion must be less favourable than when they are open. When, therefore, the

stigmata after having been open for a long time are closed at a certain moment, then the giving off of carbon dioxide from the stigmata is of course at first diminished; but as the production of carbon dioxide in the tissues continues with exactly the same speed, the carbon dioxide pressure will be a somewhat increased after a short time in the whole tracheal system, and the carbon dioxide pressure difference between the air just inside and the air just outside the almost closed stigma will soon have risen to such an extent, that the carbon dioxide delivery from the stigma will resume its original velocity.

In other words: when a stigma almost closes, the output of carbon dioxide from the tracheae will at first be decreased, but will afterwards resume its original speed. And vice versa: by the opening of a stigma that has been closed for some time, the output of carbon dioxide from the tracheae will at first be increased but after some time will resume its original velocity also in this case. The above is also applicable to the intake of oxygen.

In all probability the same is not applicable to the output of water vapour from the tracheae. While probably the production of carbon dioxide in the tissues is not dependent on the carbon dioxide pressure, the production of water vapour in the finest ramifications of the tracheal system is on the contrary highly dependent on the amount of water vapour already present. The closing of the stigmata after having been open a long time will consequently cause an increase in the relative humidity of the air in the tracheal system, and accordingly the production of new quantities of water vapour will be hampered; so we must conclude that when the stigmata are almost closed, the output of carbon dioxide will remain the same in the long run while the output of water vapour will decrease.

I think it not improbable that a decreased output of water vapour is of great importance especially to those Tracheata living in a dry atmosphere, because in this way a drying up of the tissues could be prevented.

Summary.

In the examined Tracheata the tracheae and book-lungs are generally almost closed. The stigmata are open only in so far as the exchange of the gases of respiration demands. A carbon dioxide pressure of only 2% is sufficient to cause the opening of the stigmata.

The two foremost thoracic stigmata of *Periplaneta* react independently of each other on the carbon dioxide pressure in their immediate neighbourhood.

One could call it a kind of breathing regulation, not however a regulation of the respiratory movements but a regulation of diffusion.

Laboratory of comparative Physiology.

Utrecht, January 1926.

Physics. — "On the Equation of State of Solid Substances in Connection with the General Expression for the Energy." II. By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of January 30, 1926).

I

The Equation of Energy at Higher Temperature.

1. After having established in our preceding paper ¹⁾, that the equation of state of solid substances at higher temperatures must possess the form

$$p + \frac{a}{v^2} = \frac{\lambda + RT}{v - b}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which

$$b = \frac{b_g}{1 + \frac{b_g - b_{00}}{v}} = \frac{b_g}{1 + \frac{\varphi}{v}}, \quad \text{or} \quad v - b_{00} = (v - b) \left(1 + \frac{\varphi}{v} \right), \quad . \quad (2)$$

we now proceed to the solution of the more general problem, what will be the form of the equation of state at somewhat lower temperatures, when the progressive energy of the molecules slowly begins to "degenerate", so that $L = \frac{3}{2}RT$ must be replaced by the expression of DEBYE:

$$L = \frac{3}{2}RT \left(1 + \frac{1}{20} \frac{\theta^2}{T^2} - \frac{1}{1680} \frac{\theta^4}{T^4} + \dots \right), \quad . \quad . \quad . \quad (3)$$

which holds at comparatively high temperatures (the development into series at low temperatures will be treated in Chapter IV).

This progressive Energy is half the total energy of path for solid substances (kinetic + potential energy in the paths round the positions of equilibrium of the different molecules). In the above expression the so-called zero-point energy is included. For in the general expression

$$L = \frac{9}{2} \frac{RT}{x_m^3} \int_0^{x_m} \left(\frac{1}{2} + \frac{1}{e^x - 1} \right) x^3 dx,$$

in which x is $= \frac{\beta v}{T} \left(\beta = \frac{h}{k} \right)$, and v_m represents the maximum frequency given by

$$v_m^3 = \frac{3 c^3 N}{4 \pi v},$$

¹⁾ These Proceed. 29, 95 (1926).

so that x_m is $= \frac{\beta v_m}{T}$, the term $1/2$ within the integral sign refers to the zero point energy, as immediately appears from the derivation. Execution of the integration then gives:

$$L = \frac{9/2 RT}{x_m^3} \left[\frac{1}{8} x_m^4 + \left(-\frac{1}{8} x_m^4 + \frac{1}{3} x_m^3 + \frac{1}{60} x_m^5 - \frac{1}{5040} x_m^7 + \dots \right) \right],$$

in which the first $\frac{1}{8} x_m^4$ refers to the term $\frac{1}{2}$ (hence to the zero point energy) and the form between () to the integral with $e^x - 1$. In consequence of this L becomes:

$$L = \frac{3}{2} RT \left(1 + \frac{1}{20} x_m^2 - \frac{1}{1680} x_m^4 + \dots \right),$$

which is in harmony with (3), when also

$$\theta = \beta v_m = \beta \bar{c} \sqrt[3]{\frac{3N}{4\pi v}}$$

is introduced, so that x_m becomes $= \theta : T$.

2. In the above expression for θ (the so-called "characteristic" temperature) c is the mean velocity of propagation of the elastic waves, given for solid substances by

$$\bar{c} = \frac{f}{(\sigma D)^{1/2}},$$

in which f is a pretty complicated factor containing the so-called POISSON modulus μ (into which we shall not enter any further here), σ the coefficient of compressibility $= -\frac{1}{v} \left(\frac{dv}{dp} \right)_t$, and $D = \frac{M}{v}$ the density. Then we get the following equation:

$$\theta = \beta \sqrt[3]{\frac{3N}{4\pi}} \times f \sigma^{-1/2} M^{-1/2} v^{1/2} v^{-1/2}.$$

In this $\beta = h : k = 4,77 \cdot 10^{-11}$, $\sqrt[3]{\frac{3}{4\pi}} = 0,6203$, $N = 0,6060 \cdot 10^{24}$, hence $N^{1/3} = 0,8462 \cdot 10^8$, therefore

$$\theta = 0,00250 f \cdot M^{-1/2} \sigma^{-1/2} v^{1/2}.$$

When in this $\sigma_1 = -\left(\frac{dv}{dp} \right)_t$ is substituted for $\sigma = -\frac{1}{v} \left(\frac{dv}{dp} \right)_t$, we get

$$\theta = 0,00250 f \cdot M^{-1/2} \sigma_1^{-1/2} v^{2/3},$$

in which for different metals f may lie between 0,96 ($\mu = 0,20$) and 0,37 ($\mu = 0,45$). In many cases $\mu = 1/3$, and then $f = 0,69$. If we write

$$\theta = C v^{2/3} \sigma_1^{-1/2},$$

in which therefore

$$C = 0,0025 f M^{-1/2},$$

then becomes

$$\theta^2 = C^2 v^{4/3} \sigma_1^{-1} \dots \dots \dots (4)$$

From this formula (valid for *all states of aggregation*; for liquids and gases $f=1$ in C , but then the known factor $\sqrt{c_p : c_v}$ must be added in the expression for the velocity of propagation, hence $c_p : c_v$ in C^2) θ may be successfully calculated for different metals; these values are in excellent harmony with the values calculated for them.

3. When now σ or σ_1 is calculated from the equation of state, it will at once appear that θ^2 in any case (i. e. at comparatively high temperatures) can be represented by

$$\theta^2 = \theta_a^2 \left(1 + \varphi_1 T + \frac{\varphi_2}{T} + \dots \right), \dots \dots \dots (5)$$

in which θ_a , φ_1 , φ_2 , etc. are still functions of v . In this it is of importance noteworthy, that θ^2 contains still a *term* with T , so that the above equation (3) for L after all does not give a development into series with $\frac{1}{T^2}$, $\frac{1}{T^4}$, etc., but with $\frac{1}{T}$, $\frac{1}{T^2}$, $\frac{1}{T^3}$, etc., in consequence of which a term without T will occur in L .

Substituting (5) in (3), and leaving the terms with $1 : T^3$ etc., which contain φ_2 , out of account, we get:

$$L = \frac{3}{2} RT \left(1 + \frac{A}{T} + \frac{B}{T^2} + \dots \right), \dots \dots \dots (6)$$

in which

$$A = \frac{1}{20} \theta_a^2 \varphi_1 ; \quad B = \frac{1}{20} \left(\theta_a^2 - \frac{1}{84} \theta_a^4 \varphi_1^2 \right), \dots \dots \dots (6a)$$

Hence the term in question without T is $\frac{3}{2} RA$.

II.

The Equations of Energy and of State at Higher Temperatures.

1. It is now our task to calculate from (6) and (6a) the coefficients P and Q in the general equation of state (the quantity λ , which refers to the so-called „static” virial of repulsion (see our first Paper) appears only in solid substances)

$$p + \frac{a}{v^2} = \frac{\lambda + RT \left(1 + \frac{P}{T} + \frac{Q}{T^2} + \dots \right)}{v - b}, \dots \dots \dots (7)$$

in which the development into series will also contain $\frac{1}{T}$, $\frac{1}{T^2}$, etc. We

shall see, that P , Q , etc. are related in an exceedingly simple way with A , B , etc. in the equation (6) for L , but are *by no means equal* — in contradiction with what has often been supposed.

For the calculation of P we make use of the general formula for the Energy E , viz. (the lower limits ∞ for T and v have been arbitrarily chosen, but are rational in view of the higher temperatures we are now considering)

$$E = \int_{\infty}^T c_v dT + \int_{\infty}^v \left(T \left(\frac{dp}{dt} \right)_v - p \right) dv + E_{T=\infty, v=\infty} \quad (8)$$

in which the quantity under the second integral sign (with regard to v) must be taken at $T=\infty$, i.e. at the lower limit of the *first* integral (with regard to T)¹⁾.

2. We now calculate further the quantities occurring in the second

¹⁾ For, if in general

$$du = \frac{\partial u}{\partial x} dx + \frac{\partial u}{\partial y} dy = A_{x,y} dx + B_{x,y} dy,$$

in which u is a function of x and y , du being a total differential (as is here the case with dE), we shall prove that it follows from this that

$$u_{x,y} - u_{a,b} = \int_a^x A_{x,y} dx + \int_b^y B_{a,y} dy,$$

in which, therefore, in the *second* integral x has been replaced by the *lower limit* a of the first integral. For from this latter equation follows by *total* differentiation with regard to x and y :

$$du = \frac{\partial}{\partial x} \left[\int_a^x A_{x,y} dx + \int_b^y B_{a,y} dy \right] dx + \frac{\partial}{\partial y} \left[\int_a^x A_{x,y} dx + \int_b^y B_{a,y} dy \right] dy,$$

or also

$$du = (A_{x,y} + 0) dx + \left[\int_a^x \frac{\partial A_{x,y}}{\partial y} dx + B_{a,y} \right] dy,$$

as $\frac{\partial}{\partial x} \int_b^y B_{a,y} dy = \int_b^y \frac{\partial B_{a,y}}{\partial x} dy = 0$, because $B_{a,y}$ (in which x has been substituted by a)

is independent of x . Now, however, $\frac{\partial A_{x,y}}{\partial y} = \frac{\partial B_{x,y}}{\partial x}$, according to a known property of total differentials, so that

$$du = A_{x,y} dx + \left[\int_a^x \frac{\partial B_{x,y}}{\partial x} dx + B_{a,y} \right] dy$$

hence

$$du = A_{x,y} dx + [(B_{x,y} - B_{a,y}) + B_{a,y}] dy = A_{x,y} dx + B_{x,y} dy.$$

integral of (8) from the equation of state (7). As regards c_v , as (a, b and λ independent of T)

$$E = 2L + f(v) = 2 \cdot \frac{3}{2} RT \left(1 + \frac{A}{T} + \frac{B}{T^2} + \dots \right) + \mu \cdot RT + f(v)$$

(the factor 2 only for solid; μ for multi-atomic mol.), we have immediately:

$$c_v = 2 \cdot \frac{3}{2} R \left(1 - \frac{B}{T^2} - \dots \right) + \mu R.$$

When a, b , and λ are supposed independent of T (see above),

$$\left(\frac{dp}{dt} \right)_v = \frac{R}{v-b} - \frac{R}{T^2} \frac{Q}{v-b} - \dots$$

follows from (7), hence:

$$\begin{aligned} T \left(\frac{dp}{dt} \right)_v - p &= \left(\frac{RT}{v-b} - \frac{R}{T} \frac{Q}{v-b} \right) - \left(-\frac{a}{v^2} + \frac{\lambda}{v-b} + \frac{RT}{v-b} + R \frac{P}{v-b} + \frac{R}{T} \frac{Q}{v-b} \right) \\ &= \frac{a}{v^2} - \frac{\lambda}{v-b} - R \frac{P}{v-b} - \frac{R}{T} \frac{2Q}{v-b}. \end{aligned}$$

Hence extrapolated to $T = \infty$, we have

$$\left(T \left(\frac{dp}{dt} \right)_v - p \right)_{T=\infty} = \frac{a}{v^2} - \frac{\lambda}{v-b} - R \frac{P}{v-b},$$

so that, neglecting the term μRT , the following equation may be written for (8):

$$E = 2 \cdot \frac{3}{2} R \left[(T - T_\infty) + \frac{B}{T} \right] + \left[-\frac{a}{v} - \int_{\infty}^v \frac{\lambda}{v-b} dv - R \int_{\infty}^v \frac{P}{v-b} dv \right] + E_{T=\infty, v=\infty}.$$

But in this $E_{T=\infty, v=\infty}$ is evidently $= \left[2 \cdot \frac{3}{2} RT_\infty + 2 \cdot \frac{3}{2} RA_{v=\infty} \right] + \frac{a}{v_{00}}$, be-

cause the potential energy of the attractive forces is $\frac{a}{v_{00}}$ for $v = \infty$ (for liquids and gases v_0 may be simply written), the first part referring to $2L_\infty$. (the potential energy of the ("static") repulsive forces will disappear in solid substances at $v = \infty$).

Now $A = \frac{1}{20} \theta_a^2 \varphi_1$ (see above), and as we shall see presently (in Chapter III),

g. e. d. (It can, likewise, be proved that from $du = A_{x,y} dx + B_{x,y} dy$ follows $u_{x,y} - u_{a,b} = \int_a^x A_{x,b} dx + \int_b^y B_{x,y} dy$, in which inside the first integral y has been replaced by the lowest limit b of the second integral).

When this is applied to the well-known equation $dE = c_v dT + \left[T \left(\frac{dp}{dt} \right)_v - p \right] dv$, equation (8) ensures naturally.

this is $=0$ at $v=\infty$ (on account of the factor $v^{-2/3}$; see (14) and (15)). Hence we have finally:

$$E = \left(\frac{a}{v_{00}} - \frac{a}{v} \right) - \int_{\infty}^v \frac{\lambda}{v-b} dv + 2 \cdot \frac{3}{2} RT \left(1 + \frac{B}{T^2} \right) - R \int_{\infty}^v \frac{P}{v-b} dv.$$

But according to (6) is also:

$$E = \left(\frac{a}{v_{00}} - \frac{a}{v} \right) - \int_{\infty}^v \frac{\lambda}{v-b} dv + 2 \cdot \frac{3}{2} RT \left(1 + \frac{A}{T} + \frac{B}{T^2} \right). \quad (9)$$

where $2L$ has been increased by the potential energy of the attractive forces and (in solid substances) by that of the „static” repulsive forces¹⁾, so that

$$2 \cdot \frac{3}{2} RA = -R \int_{\infty}^v \frac{P}{v-b} dv$$

1) To prevent the potential energy from becoming $=\infty$ at finite values of v , it would be better to substitute $\frac{\lambda}{v}$ for λ in the equation of state. The expression

$$\begin{aligned} \int_{\infty}^v \frac{\lambda}{v-b} dv &= \int_{\infty}^v \frac{\lambda}{v-b_{00}} \left(1 + \frac{\varphi}{v} \right) dv = \lambda \left(\log(v-b_{00}) + \frac{\varphi}{b_{00}} \log \frac{v-b_{00}}{v} \right) = \\ &= \lambda \left(\log \frac{v-b_{00}}{\infty} + \frac{\varphi}{b_{00}} \log \frac{v-b_{00}}{v} \right) = \lambda \left[\log \frac{(v-b)(1+\varphi/v)}{\infty} + \right. \\ &\quad \left. + \frac{\varphi}{b_{00}} \log \left(\frac{v-b}{v} \left(1 + \frac{\varphi}{v} \right) \right) \right], \end{aligned}$$

which would be $=-\infty$ for all finite values of v , becomes with $\frac{\lambda}{v}$:

$$\begin{aligned} \int_{\infty}^v \frac{\lambda}{v(v-b)} dv &= \int_{\infty}^v \frac{\lambda}{v(v-b_{00})} \left(1 + \frac{\varphi}{v} \right) dv = \\ &= \lambda \left[\frac{1}{b_{00}} \log \frac{v-b_{00}}{v} + \varphi \int_{\infty}^v \left(-\frac{1}{b_{00}v^2} + \frac{1}{b_{00}^2} \left(\frac{1}{v-b_{00}} - \frac{1}{v} \right) \right) dv \right] = \\ &= \lambda \left[\frac{1}{b_{00}} \log \frac{v-b_{00}}{v} + \frac{\varphi}{b_{00}^2} \left(\frac{b_{00}}{v} + \log \frac{v-b_{00}}{v} \right) \right], \end{aligned}$$

which now remains finite for finite values of v , as it should.

In consequence of the substitution of $\frac{\lambda}{v}$ for λ (which has practically very little influence for solid substances (at $p=0$) on the different calculations, because v varies only little between the melting-point of solid substances and $T=0$), not λ stands next to RT , in (1), but $\frac{\lambda}{v}$, in consequence of which $-RT$ being of the dimensions of $\frac{a}{v} - \lambda$ now becomes analogous to a , and not to $\frac{a}{v}$.

must be found. A will, therefore, have to disappear for $v = \infty$ (see above), and we have for the quantity P in the equation of state (7):

$$\underline{P = -2 \cdot \frac{3}{2} (v-b) \frac{dA}{dv}} \quad \dots \quad (10)$$

In this A is $= \frac{1}{20} \theta_a^2 \varphi_1$ according to (6^a), and we shall therefore have to calculate $\theta_a^2 \varphi_1$ (in Chapter III). It may still be mentioned, that the quantities λ and a can never be determined by means of thermodynamic relations; these quantities can only be calculated on the basis of molecular-theoretical considerations.

3. For the calculation of Q, S, U etc. in (7) we start from the well-known equation

$$T \left(\frac{d^2 p}{dt^2} \right)_v = \left(\frac{dc_v}{dv} \right)_t \dots \dots \dots (11)$$

In this is, according to (7):

$$\left(\frac{dp}{dt} \right)_v = \frac{R}{v-b} - \frac{1}{T^2} \frac{R}{v-b} \frac{Q}{v-b} - \frac{2R}{T^3} \frac{S}{v-b} - \frac{3R}{T^4} \frac{U}{v-b} - \dots$$

hence

$$T \left(\frac{d^2 p}{dt^2} \right)_v = \frac{1.2R}{T^2} \frac{Q}{v-b} + \frac{2.3R}{T^3} \frac{S}{v-b} + \frac{3.4R}{T^4} \frac{U}{v-b} + \dots$$

Further follows from $c_v = 2 \cdot \frac{3}{2} R \left(1 - \frac{1B}{T^2} - \frac{2C}{T^3} - \frac{3D}{T^4} - \dots \right)$:

$$\left(\frac{dc_v}{dv} \right)_t = -2 \cdot \frac{3}{2} R \left(\frac{1}{T^2} \left(\frac{dB}{dv} \right)_t + \frac{2}{T^3} \left(\frac{dC}{dv} \right)_t + \frac{3}{T^4} \left(\frac{dD}{dv} \right)_t \right).$$

We find, therefore, immediately:

$$\underline{Q = -2 \cdot \frac{3}{2} \frac{v-b}{2} \frac{dB}{dv}}; \quad \underline{S = -2 \cdot \frac{3}{2} \frac{v-b}{3} \frac{dC}{dv}}; \quad \underline{U = -2 \cdot \frac{v-b}{4} \frac{dD}{dv}} \quad (12)$$

which expressions are in perfect harmony with (10). The factor 2 disappears for liquids and gases.

The quantities P, Q, S, U , etc. in the equation of state

$$p + \frac{a}{v^2} = \frac{1}{v-b} \left[\lambda + RT \left(1 + \frac{P}{T} + \frac{Q}{T^2} + \frac{S}{T^3} + \frac{M}{T^4} + \dots \right) \right],$$

in which the quantity λ only appears in solid substances, are therefore *not equal* to the corresponding quantities A, B, C, D , etc. of the equation of Energy

$$E = 2 \cdot \frac{3}{2} RT \left(1 + \frac{A}{T} + \frac{B}{T^2} + \frac{C}{T^3} + \frac{D}{T^4} + \dots \right) + \text{Pot. Energy},$$

but there is a simple relation between them (expressed by 10) and (12)¹⁾.

III.

Calculation of $A = \frac{1}{20} \theta_a^2 \varphi_1$ and $\frac{dA}{dv}$ at Higher Temperatures.

1. For the calculation of $\theta_a^2 \varphi_1$ in (5), viz. $\theta^2 = \theta_a^2 (1 + \varphi_1 T)$, we must determine $\theta^2 = C^2 v^{4/3} \sigma_1^{-1}$ according to (4). But for this it is necessary in the first place to know the value of $\sigma_1 = -\left(\frac{dp}{dv}\right)_t$. Taking (10) into account, the equation of state becomes:

$$p = -\frac{a}{v^2} + \frac{\lambda + RT}{v - b} - 2 \cdot \frac{3}{2} R \frac{dA}{dv} \dots = -\frac{a}{v^2} + \frac{\lambda + RT}{v - b_{00}} \left(1 + \frac{\varphi}{v} \right) - 2 \cdot \frac{3}{2} R \frac{dA}{dv} \dots$$

from which follows:

$$\left(\frac{dp}{dv}\right)_t = \frac{2a}{v^3} - (\lambda + RT) \left(\frac{1 + \varphi/v}{(v - b_{00})^2} + \frac{\varphi/v^2}{v - b_{00}} \right) - 2 \cdot \frac{3}{2} R \frac{d^2 A}{dv^2} \dots$$

hence

$$\sigma_1^{-1} = -\left(\frac{dp}{dv}\right)_t = \left[-\frac{2a}{v^3} + 2 \cdot \frac{3}{2} R \frac{d^2 A}{dv^2} + \frac{\lambda}{(v - b_{00})^2} \left(1 + \frac{\varphi}{v} + \frac{\varphi v - b_{00}}{v} \right) \right] + \frac{RT}{(v - b_{00})^2} \left(1 + \frac{\varphi}{v} + \frac{\varphi v - b_{00}}{v} \right),$$

so that from $\theta^2 = C^2 v^{4/3} \sigma_1^{-1} = \theta_a^2 (1 + \varphi_1 T)$ follows:

$$\theta_a^2 = C^2 v^{4/3} \left[-\frac{2a}{v^3} + 2 \cdot \frac{3}{2} R \frac{d^2 A}{dv^2} + \frac{\lambda}{(v - b_{00})^2} \left(1 + \frac{\varphi}{v} + \frac{\varphi v - b_{00}}{v} \right) \right],$$

and

$$\theta_a^2 \varphi_1 = C^2 R \frac{v^{4/3}}{(v - b_{00})^2} \left(1 + \frac{\varphi}{v} + \frac{\varphi v - b_{00}}{v} \right). \quad (13)$$

From $A = \frac{1}{20} \theta_a^2 \varphi_1$ follows therefore:

$$\frac{dA}{dv} = \frac{1}{20} C^2 R \left[\left(\frac{4}{3} \frac{v^{1/3}}{(v - b_{00})^2} - 2 \frac{v^{4/3}}{(v - b_{00})^3} \right) \left(1 + \frac{\varphi}{v} + \frac{\varphi v - b_{00}}{v} \right) - \frac{v^{4/3}}{(v - b_{00})^2} \left(\frac{\varphi}{v^2} + \frac{\varphi v - b_{00}}{v^2} + \frac{\varphi}{v} \left(\frac{v - b_{00}}{v^2} - \frac{1}{v} \right) \right) \right],$$

¹⁾ Expressions, as among others have been drawn up by K. BENNEWITZ, Z. f. phys. Ch. 110, p. 725 (1924), i. e. (for ideal gases) $p v = RT \left(1 + \frac{U}{E_0} \right)$, and by many others, must therefore be absolutely rejected.

or

$$\frac{dA}{dv} = \frac{1}{20} C^2 R \frac{v^{1/3}}{(v-b_{00})^2} \left[\left(\frac{4}{3} - 2 \frac{v}{v-b_{00}} \right) \left(1 + \frac{\varphi}{v} + \frac{\varphi}{v} \frac{v-b_{00}}{v} \right) - 2 \frac{\varphi}{v} \frac{v-b_{00}}{v} \right],$$

or also with $\frac{v-b_{00}}{v} = z'$ and $\frac{\varphi}{v} = \omega$:

$$\frac{dA}{dv} = \frac{1}{20} C^2 R \frac{v^{1/3}}{(v-b_{00})^2} \left[\left(\frac{4}{3} - \frac{2}{z'} \right) + \omega \left(\left(\frac{4}{3} - \frac{2}{z'} \right) (1+z') - 2z' \right) \right],$$

i.e.

$$\frac{dA}{dv} = \frac{1}{20} C^2 R v^{-2/3} \frac{v}{(v-b_{00})^2} \left[\left(\frac{4}{3} - \frac{2}{z'} \right) - \omega \left(\frac{2}{3} + \frac{2}{z'} + \frac{2}{3} z' \right) \right].$$

With $v-b_{00} = (v-b)(1+\omega)$ and $\frac{v-b}{v} = z$ we get $z' = z(1+\omega)$,

hence

$$\frac{dA}{dv} = \frac{1}{20} C^2 R v^{-2/3} \frac{v}{(v-b)^2 (1+\omega)^2} \left[\frac{4}{3} - \frac{2}{z} \frac{1}{1+\omega} - \omega \left(\frac{2}{3} + \frac{2}{z} \frac{1}{1+\omega} + \frac{2}{3} z(1+\omega) \right) \right],$$

or

$$\frac{dA}{dv} = \frac{1}{20} C^2 R v^{-2/3} \frac{v^2}{(v-b)^3 (1+\omega)^3} \left[\frac{4}{3} z(1+\omega) - 2 - \omega \left(\frac{2}{3} z(1+\omega) + 2 + \frac{2}{3} z^2 (1+\omega)^2 \right) \right],$$

so that we get with $-2 - 2\omega = -2(1+\omega)$:

$$-(v-b) \frac{dA}{dv} = \frac{1}{10} \frac{C^2 R v^{-2/3}}{z^2 (1+\omega)^2} \left(1 - \frac{1}{3} z(2-\omega) + \frac{1}{3} z^2 \omega (1+\omega) \right). \quad (\alpha)$$

From this we see, that the calculation of $\frac{d^2 A}{dv^2}$, occurring in θ_a^2 , will become very complicated, so that we will omit the calculation of Q , in which $\frac{dB}{dv}$ occurs, because B contains θ_a^2 according to (6^a). And the same thing applies to the following coefficients in a still greater degree, where, besides, the coefficients φ_2 etc. would have to be calculated according to (5). For $A = \frac{1}{20} \theta_a^2 \varphi_1$ we found above according to (13):

$$A = \frac{1}{20} C^2 R v^{-2/3} \frac{v^2}{(v-b_{00})^2} \left(1 + \omega + \omega \frac{v-b_{00}}{v} \right),$$

or with $v-b_{00} = (v-b)(1+\omega)$, $\frac{v-b}{v} = z$:

$$A = \frac{1}{20} \frac{C^2 R v^{-2/3}}{z^2 (1+\omega)} (1+\omega z). \quad (\beta)$$

Putting

$$\underline{A_0 = \frac{1}{20} \frac{C^2 R v^{-2/3}}{z^2 (1+\omega)^2}} \quad (14)$$

we get according to (a), (β) and (10):

$$A = A_0(1+\omega)(1+\omega z) ; \quad P = 2.3 A_0 \left(1 - \frac{1}{3} z(2-\omega) + \frac{1}{3} z^2 \omega(1+\omega) \right), \quad (15)$$

through which the quantity P of the equation of state

$$\left(p + \frac{a}{v^2} \right) (v-b) = \lambda + RT \left(1 + \frac{P}{T} \right)$$

is expressed in the quantity A of the equation of Energy

$$E = 2. \frac{3}{2} RT \left(1 + \frac{A}{T} \right) + \text{Pot. Energy.}$$

As we already remarked in Chapter II: P is *by no means equal to* A , and this will also apply to the following coefficients. Only in the case of ideal gases (see further below) the different coefficients would become equal to each other ($z=1$, $\omega=0$), thus $A=P=A_0$ (the factor 2 in P (and E) appears only in solid substances).

2. In *ordinary liquids* (e.g. in benzene) $z = \frac{1}{14}$ and $\omega = 2 \frac{1}{7}$ in the neighbourhood of the point of solidification (5.5°C.), hence

$$A = 3,624 A_0 ; \quad P = 3,045 A_0.$$

In *molten copper* $z = \frac{1}{38.2}$, $\omega = 2$ at 1083°C. , through which A and P become:

$$A = 3,157 A_0 ; \quad P = 3,004 A_0.$$

And in *solid copper* $z = \frac{1}{6}$, $\omega = 0.6$, (20°C.), hence

$$A = 1,760 A_0 ; \quad P = 5,587 A_0.$$

Accordingly in the two liquids mentioned, P is only slightly smaller than A , whereas in solid copper P is more than 3 times as great as A .

Let us now determine the different values of A_0 according to the above expression (14). C being $= 0.0025 f \times M^{-1/2}$ (see I, § 1), $C^2 v^{-2/3} = 6 \frac{1}{4} \cdot 10^{-6} \cdot M^{-5/3} D^{2/3}$ with $f=1$, because $v = M:D$. Therefore in *liquid benzene* (5.5°C.):

$$C^2 R v^{-2/3} = 6 \frac{1}{4} \cdot 10^{-6} \times 83.17 \cdot 10^6 \times (78.05)^{-5/3} \times (0.9)^{2/3} = 519.8 : 1425 \times \\ \times 0.9322 = 0.3400.$$

Hence

$$A_0 = \frac{1}{20} \times 0.3400 \times (14)^2 : \left(3 \frac{1}{7} \right)^2 = 0.3373.$$

In *molten copper* at 1083°C. we have:

$$C^2 R v^{-2/3} = 519,8 \times (63,57)^{-5/3} \times (8,40)^{2/3} = 519,8 : 1013 \times 4,132 = 2,121,$$

so that we get:

$$A_0 = \frac{1}{20} \times 2,121 \times (38,23)^2 : 3^2 = 17,22.$$

In solid copper (20° C.) evidently

$$C^2 R v^{-2/3} = 2,121 \times \left(\frac{8,933}{8,40} \right)^{2/3} = 2,121 \times 1,042 = 2,210,$$

in consequence of which becomes

$$A_0 = \frac{1}{20} \times 2,210 \times (6)^2 : (1,6)^2 = 1,554.$$

We then get finally:

liquid Benzene (5°,5 C.)	$A = 1,22^2$	$P = 1,02^7$	$\frac{A}{T} = \frac{1}{228}$	$\frac{P}{T} = \frac{1}{271}$
molten Copper (1083° C.)	$A = 54,3^6$	$P = 51,7^3$	$\frac{A}{T} = \frac{1}{25}$	$\frac{P}{T} = \frac{1}{26}$
solid Copper (20° C.)	$A = 2,73^5$	$P = 8,68^2$	$\frac{A}{T} = \frac{1}{107}$	$\frac{P}{T} = \frac{1}{34}$

In substances as *benzene* the correction in the equation of state is accordingly only about 0,4 % at $T = \frac{1}{2}$, but in liquid $\left(T = \frac{1}{3} T_k \right)$ and in solid $\left(T = \frac{1}{15} T_k \right)$ copper already resp. 4 % and 3 %, hence about 10 or 8 times greater. But in the calculation of C we took above the factor $f = 1$. In liquid benzene and copper $f^2 = c_p : c_v$ is only slightly greater than the unit, but in solid copper f^2 will become = 0,4 (with $\mu = 0,36$, $f = 0,63$). Consequently $\frac{P}{T}$ becomes only = $\frac{1}{85}$, i.e. 1,2 % instead of $\frac{1}{34} = 3$ %.

In gases, where v is so many times greater than in liquids, the correction $P : T$ will appear to be a great many times smaller at the same temperature, and even approach 0. The quantity $\omega = \varphi : v$ can be put = 0, whereas z becomes = $(v - b) : v = 1$. In consequence of this we get for gases simply:

$$A = A_0; \quad P = 3A_0 \left(1 - \frac{1}{3} \cdot 2 \right) = A_0.$$

If in benzene vapour v is taken 1000-times greater than in liquid benzene, A_0 becomes:

$$A_0 = \frac{1}{20} C^2 R v^{-2/3} = \frac{1}{20} \times 0,3400 : (1000)^{2/3} = 0,00017;$$

hence at $T = \text{about } 280^\circ$ absolute the correction quantity $\frac{P}{T}$ will become $= 0,6 \cdot 10^{-6}$, i. e. perfectly negligible. And the following terms with Q will appear to be still much smaller.

IV.

The Equations of Energy and State at very Low Temperatures.

The development into series (3) is now replaced by the DEBYE development holding only at very low temperatures

$$E_t = \frac{9}{8} R \theta_0 + \frac{3}{5} \frac{R \pi^4}{\theta^3} T^4 - \dots \quad (16)$$

when by E_t we represent the temperature part of the Energy. For the total Energy the potential energy of the attractive and repulsive forces of static nature (see Chapter II) have to be added. The expression (16) applies to *solid* substances; the question in how far it is also applicable to liquids and gases at *very low* temperatures, and whether in these cases we have to do with open or closed paths (in the former case we should have still to divide by 2) may be left undecided for the present.

Now the zero point energy $\frac{9}{8} R \theta_0$ remains *outside* the terms with T^4, T^8 etc. Of course θ_0 should be put in it and not θ , because with the cor-

responding term $\frac{9RT}{x_m^3} \int_0^{x_m} \frac{1}{2} x^3 dx = \frac{9}{8} RT x_m$ the quantity $T x_m = \beta v_m = \theta$

will refer to $T=0$ according to the definition (since this term must represent the energy at $T=0$). The quantity v_m , hence also θ , however, remains a function of v .

From the equation of state (see further below) the following equation will follow as an analogon to (5):

$$\theta^2 = \theta_0^2 (1 + \varphi_1 T^4 \dots), \quad (17)$$

so that we get:

$$E_t = \frac{9}{8} R \theta_0 + \frac{3}{5} \frac{R \pi^4}{\theta_0^3 (1 + \varphi_1 T^4 \dots)^{3/2}} T^4 - B T^8 \dots$$

i. e.

$$E_t = \frac{9}{8} R \theta_0 + \frac{3}{5} \frac{R \pi^4}{\theta_0^3} \left(1 - \frac{3}{2} \varphi_1 T^4 \dots \right) T^4 - B T^8 \dots$$

Confining ourselves, therefore, to terms with T^4 , the following equation remains:

$$\underline{E_t = \frac{9}{8} R \theta_0 + \frac{3}{5} \frac{R \pi^4}{\theta_0^3} T^4 = \frac{9}{8} R \theta_0 + A T^4.} \quad (18)$$

Instead of (7) we may write for the equation of state:

$$p + \frac{a}{v^2} = \frac{\lambda + PT^4 \dots}{v-b}, \quad \dots \quad (19)$$

in which we shall try to express P in A . For this purpose we start again from the formula

$$T \left(\frac{d^2 p}{dt^2} \right) = \left(\frac{dc_v}{dv} \right)_t$$

giving

$$\frac{12 PT^3}{v-b} = \frac{d}{dv} (4 AT^3)_t = 4 T^3 \left(\frac{dA}{dv} \right)_t$$

from which follows:

$$P = \frac{1}{3} (v-b) \left(\frac{dA}{dv} \right)_t \quad \dots \quad (20)$$

2. As A depends on v through θ_0 , we must again determine the quantity $\theta^2 = C^2 v^{4/3} \sigma_1^{-1}$, i.e. $\sigma_1^{-1} = - \left(\frac{dp}{dv} \right)_t$. From (19), i.e. $\left(\text{with } \frac{1}{v-b} = \frac{1}{v-b_{00}} \left(1 + \frac{\varphi}{v} \right) \right)$

$$p = - \frac{a}{v^2} + \frac{\lambda + PT^4}{v-b_{00}} \left(1 + \frac{\varphi}{v} \right),$$

follows

$$\left(\frac{dp}{dv} \right)_t = \frac{2a}{v^3} - \frac{\lambda}{(v-b_{00})^2} \left(1 + \frac{\varphi}{v} + \frac{\varphi}{v} \frac{v-b_{00}}{v} \right) + T^4 \frac{d}{dv} \left(\frac{P}{v-b} \right)_t$$

which (with (20)) passes into

$$\left(\frac{dp}{dv} \right)_t = \frac{2a}{v^3} - \frac{\lambda}{(v-b_{00})^2} \left(\quad \right) + \frac{1}{3} T^4 \left(\frac{d^2 A}{dv^2} \right)_t$$

so that we get:

$$\theta^2 = C^2 v^{4/3} \left[- \frac{2a}{v^3} + \frac{\lambda}{(v-b_{00})^2} \left(\quad \right) - \frac{1}{3} T^4 \left(\frac{d^2 A}{dv^2} \right)_t \right],$$

consequently

$$\theta_0^2 = C^2 v^{4/3} \left[- \frac{2a}{v^3} + \frac{\lambda}{(v-b_{00})^2} \left(1 + \frac{\varphi}{v} + \frac{\varphi}{v} \frac{v-b_{00}}{v} \right) \right] \quad \dots \quad (a)$$

As according to (18) $A = \frac{3}{5} \frac{R\pi^4}{\theta_0^3}$, we have $\left(\frac{dA}{dv} \right)_t = - \frac{9}{5} \frac{R\pi^4}{\theta_0^4} \left(\frac{d\theta_0}{dv} \right)_t$.

But from (a) follows:

$$2\theta_0 \left(\frac{d\theta_0}{dv} \right)_t = C^2 \left[\frac{10}{3} \frac{a}{v^{8/3}} + \lambda \frac{d}{dv} \left(\frac{v^{4/3}}{(v-b_{00})^2} \left(1 + \frac{\varphi}{v} + \frac{\varphi}{v} \frac{v-b_{00}}{v} \right) \right)_t \right].$$

The last differentiation has already been carried out in § 1 of Chapter III

in the expression (a), when this is divided by $-\frac{1}{20} C^2 R (v-b)$. Hence we get:

$$2\theta_0 \left(\frac{d\theta_0}{dv} \right) = C^2 \left[\frac{10}{3} \frac{a}{v^{5/3}} - 2\lambda \frac{v^{-2/3}}{(v-b)z^2(1+\omega)^2} \left(1 - \frac{1}{3} z(2-\omega) + \frac{1}{3} z^2 \omega(1+\omega) \right) \right],$$

or also

$$2\theta_0 \left(\frac{d\theta_0}{dv} \right)_t = \frac{C^2}{v^{5/3}} \left[\frac{10}{3} \frac{a}{v} - 2\lambda \frac{\lambda}{z^3(1+\omega)^2} \left(1 - \frac{1}{3} z(2-\omega) + \frac{1}{3} z^2 \omega(1+\omega) \right) \right],$$

as $\frac{v-b}{v} = z$. We have, therefore:

$$\left(\frac{dA}{dv} \right)_t = \frac{9}{5} \frac{R\pi^4}{\theta_0^5} \frac{C^2}{v^{5/3}} \left[-\frac{5}{3} \frac{a}{v} + \frac{\lambda}{z^3(1+\omega)^2} \left(\quad \right) \right].$$

In this θ_0^2 has been given by (a), consequently (cf. § 1 of Chapter III) by

$$\theta_0^2 = C^2 v^{4/3} \left[-\frac{2a}{v^3} + \frac{\lambda}{(v-b)^2(1+\omega)} (1+\omega z) \right],$$

i. e.

$$\theta_0^2 = \frac{C^2}{v^{2/3}} \left[-\frac{2a}{v} + \lambda \frac{1+\omega z}{z^2(1+\omega)} \right] \dots \dots \dots (21)$$

We find, therefore, for P according to (20):

$$P = \frac{3}{5} \frac{R\pi^4}{\theta_0^5} C^2 \frac{v-b}{v^{5/3}} \left[-\frac{5}{3} \frac{a}{v} + \frac{\lambda}{z^3(1+\omega)^2} \left(1 - \frac{1}{3} z(2-\omega) + \frac{1}{3} z^2 \omega(1+\omega) \right) \right].$$

And as

$$A = \frac{3}{5} \frac{R\pi^4}{\theta_0^3} \dots \dots \dots (22)$$

(see above), we finally get with $(v-b): v = z$ and θ_0^2 according to (21):

$$P = A z \frac{-\frac{5}{3} \frac{a}{v} + \frac{\lambda}{z^3(1+\omega)^2} \left(1 - \frac{1}{3} z(2-\omega) + \frac{1}{3} z^2 \omega(1+\omega) \right)}{-2 \frac{a}{v} + \frac{\lambda}{z^2(1+\omega)} (1+\omega z)} \dots (23)$$

If, therefore, A is known through (22), combined with (21), P can be calculated from (23). Again — no more than at high temperatures — the coefficient P of the equation of state is *not* equal to the corresponding coefficient A of the equation of energy.

3. We will now carry out the calculation for the case of *solid* copper at very low temperatures. We know that the quantity λ is determined by

$$\lambda = \frac{a}{v_0^2} (v_0 - b_0) = \frac{a}{v_0} \frac{v_0 - b_0}{v_0} = \frac{a}{v_0} z_0,$$

as immediately appears from the equation of state (19), when (at $p=0$) v approaches to v_0 . In the neighbourhood of $T=0$ z and z_0 , ω and ω_0 , v and v_0 may be put equal to each other without the slightest hesitation. For already at comparatively high temperatures, e. g. at 20°C. , the difference is inappreciable; at 20°C. $v=7,12$ and $v_0=7,05$; $z=(v-b)$: $v=1,18^6:7,11^6=1:6,00$ and $z_0=1,13^8:7,04^6=1:6,19^2$ (see Chapter II of our first Paper), so that the differences between these quantities at T in the neighbourhood of T_0 and at T_0 itself will no doubt be quite negligible.

If, therefore, we write simply $\lambda = \frac{a}{v} z$ with omission of the indices 0, then

$$\left. \begin{aligned} \theta_0^2 &= \frac{C^2 a}{v^{2/3} v} \frac{1-z(2+\omega)}{z(1+\omega)} \\ P &= A \frac{1 - \frac{1}{3} z(2-\omega) - \frac{1}{3} z^2(1+\omega)(5+4\omega)}{(1+\omega)(1-z(2+\omega))} \end{aligned} \right\} \quad (24)$$

With $z=1:6,19^2$, $\omega=0,6 \times (7,116:7,046)=0,6060$ this becomes:

$$\left. \begin{aligned} \theta_0^2 &= 2,233 \frac{C^2 a}{v^{2/3} v} \\ P &= 0,8830 A \end{aligned} \right\}$$

In this $C^2 : v^{2/3} = 6 \frac{1}{4} \cdot 10^{-6} \times (63,57)^{-1} \times (7,046)^{-2/3} \times 0,3969$, because in C^2 the factor f^2 is $= (0,63)^2 0,3969$ (see § 2 of Chapter III). Hence $C^2 : v^{2/3} = 0,01062 \cdot 10^{-6}$ is found. Further $\frac{a}{v} = 32,63 \cdot 10^{12} : 7,046 = 4,631 \cdot 10^{12}$, so that for θ_0^2 is found:

$$\theta_0^2 = 2,233 \times 0,01062 \cdot 10^{-6} \times 4,631 \cdot 10^{12} = 0,1098 \cdot 10^6,$$

so that $\theta_0 = 331,3$, $\theta_0^3 = 36,38 \cdot 10^6$.

Therefore, according to (22):

$$A = \frac{3}{5} \frac{83,17 \cdot 10^6 \times 97,41}{36,38 \cdot 10^6} = 133,6; \quad P = 118,0.$$

According to (16) and (19) we have therefore for solid copper in the neighbourhood of $T=0$:

$$\left. \begin{aligned} E_t &= \frac{9}{8} R \theta_0 + 134 T^4 \\ p + \frac{a}{v^2} &= \frac{\lambda + 118 T^4}{v-b} \end{aligned} \right\}$$

In this the zero-point energy $\frac{9}{8} R \theta_0 = \frac{9}{8} \times 83,17 \cdot 10^6 \times 331,3 =$

$$= 0,03100 \cdot 10^{12}, \lambda \text{ being } = \frac{a}{v} \times z = 4,631 \cdot 10^{12} : 6,192 = 0,7479 \cdot 10^{12}.$$

Hence we have:

$$\left. \begin{aligned} E_t &= 0,031 \cdot 10^{12} + 134 T^4 \\ \left(p + \frac{a}{v^2}\right)(v-b) &= 0,75 \cdot 10^{12} + 118 T^4 \end{aligned} \right\} \begin{array}{l} \text{Solid copper} \\ T=0 \end{array} \quad (25)$$

If $T=20^\circ$ absolute, the equations become:

$$\left. \begin{aligned} E_t &= 0,031 \cdot 10^{12} + 21,4 \cdot 10^6 \\ \left(p + \frac{a}{v^2}\right)(v-b) &= 0,75 \cdot 10^{12} + 18,9 \cdot 10^6 \end{aligned} \right\} (T=20^\circ \text{ abs.})$$

so that the first terms are then still resp. 1450 and 40000 times greater than the terms with T^4 . Hence at 20° abs. the temperature energy is already almost equal to the zero point energy, the temperature exercising hardly any influence in the equation of state, so that the coefficient of expansion has become exceedingly small.

4. For the calculation of the *coefficient of expansion* in the neighbourhood of $T=0$ we start from the known expression

$$\left(\frac{dp}{dt}\right)_v = -\left(\frac{dp}{dv}\right)_t \times \left(\frac{dv}{dt}\right)_p = v\sigma_1^{-1} \times \frac{1}{v} \left(\frac{dv}{dt}\right)_p$$

From this follows:

$$\alpha = \frac{1}{v} \left(\frac{dv}{dt}\right)_p = \frac{\left(\frac{dp}{dt}\right)_v}{v\sigma_1^{-1}}.$$

In this $\left(\frac{dp}{dt}\right)_v$ is according to (19) $= \frac{4PT^3}{v-b} = \frac{471,9}{1,138} T^3 = 414,7 T^3$. And θ_2^0 being $= C^2 v^{4/3} \sigma_1^{-1}$, $v\sigma_1^{-1} = \theta_2^0 : C^2 v^{1/3}$. For $C^2 : v^{2/3}$ we found above the value $0,01062 \cdot 10^{-6}$, so that $C^2 v^{1/3}$ becomes $= 0,01062 \cdot 10^{-6} \times v = 0,01062 \cdot 10^{-6} + 7,046 = 0,07483 \cdot 10^{-6}$. Hence we calculate $0,1098 \cdot 10^6 : 0,07483 \cdot 10^{-6} = 1,467 \cdot 10^{12}$ for $v\sigma_1^{-1}$. Thus

$$10^6 \alpha = \frac{414,7 T^3}{1,467 \cdot 10^6} = \frac{282,6 \cdot 10^{-6} T^3}{(T=0)}.$$

For the *specific heat* follows from (25):

$$c_v = 534,4 T^3 \text{ abs. units.}$$

But as 1 gr. cal. $= 41,86^3 \cdot 10^6$ Ergs, c_v becomes

$$c_v = \frac{12,77 \cdot 10^{-6} T^3}{\text{gr. cal. } (T=0)}.$$

According at very low temperatures the coefficient of expansion runs entirely parallel with the atomic heat, but is *numerically* (i. e. $10^6 \alpha$) 22,14 times greater than c_v expressed in gr. cal.

At 20°

$$10^6 \alpha = \underline{2,261} \quad ; \quad c_v = \underline{0,1021} (T=20^\circ \text{ abs.})$$

would be according to the above. At $20^{\circ}, 7$ abs. $c_v = 0.122$ has been found according to KEESOM and K. ONNES¹⁾. This is in pretty good agreement, for c_v must be $= 0.102 \times \left(\frac{20,7}{20}\right)^3 = 0.102 \times 1.11 = 0.113$ at $20,7^{\circ}$. Also

the coefficient of expansion can be right, for $3 \times 3,9 = 11,7$ has been found by LINDEMANN between 20° and 80° abs., while $10^6 \alpha = 3 \times 6,8 = 20,4$ at 85° (there the T -law is no longer valid), so that duly 11.7 lies intermediate between 2.26 and 20.4 (the mean value would be 11.3).

We remark that at 20° C. ($T = 293$) $10^6 \alpha = 3 \times 17 = 51$, and c_v is $= 5.8$. The coefficient of expansion $10^6 \alpha$ is at these higher temperatures numerically only 8.8 times greater than c_v in gr. cal., against 22.1 times at very low temperatures (see above).

5. Above in (24) we found for θ_0^2 an expression, which is quite identical with that found by us in our first paper (see chapter V, equation (8) for $\sigma^{-1} = v\sigma_1^{-1}$) at higher temperatures for $\theta^2 = C^2 v^{4/3} \sigma_1^{-1}$. This is self-evident, because, as appears from the derivation, at higher temperatures $\lambda + RT$ has been replaced by its value $\frac{a}{v^2} (v-b)$ from the equation

of state ($p=0$), the same thing having been done above with ($p=0$) $\lambda = \frac{a}{v_0^2} (v_0 - b_0)$, while $T=0$ was put. Through this the expressions for θ^2 (with T) and θ_0^2 (with $T=0$) have become identical; with this difference, however, that the values of v will be slightly different in the two cases. Consequently at 20° C. with $z = 1:6,00$, $\omega = 0,6$ is obtained $\theta^2 = 2,125 \frac{C^2 a}{v^{2/3} v}$ instead of $2,233 \times \text{ibid}$ (see above). We have therefore:

$$\theta^2 : \theta_0^2 = \frac{2,125}{(7,116)^{5/3}} : \frac{2,233}{(7,046)^{5/3}} = \frac{2,125}{2,233} \times \left(\frac{7,046}{7,116}\right)^{5/3},$$

i.e.

$$\theta_0^2 (T=0) = \theta^2 (20^{\circ} \text{ C.}) \times 1,051 \times (1,010)^{5/3} = \theta_{(20^{\circ} \text{ C.})}^2 \times 1,068.$$

And as $\theta_0 (T=0) = 331.3$ was found (see § 3), θ will be $331.3 : 1.034 = 320.6$ at 20° C ($= 293^{\circ}$ abs.)²⁾. The difference in value at $T=0$ and $T=293^{\circ}$ is therefore small.

And the same thing will be the case with the coefficient of compressibility σ . As $\theta^2 = C^2 v^{4/3} \sigma_1^{-1} = C^2 v^{1/3} \times v\sigma_1^{-1}$, the values of $v\sigma_1^{-1} = -v \frac{dp}{dv}$ will be to each other as those of $\theta^2 : v^{1/3}$, i.e. those of $\sigma = -\frac{1}{v} \frac{dv}{dp}$ as those of $v^{1/3} : T^2$. Hence

$$\sigma : \sigma = (1,010)^{1/3} \times 1,068 = 1,072.$$

¹⁾ Comm. 147a, p. 8 (1915).

²⁾ KEESOM and KAMERLINGH ONNES (Comm. 143, 1914) have found between 15° and 22° abs. the value 323.5. Later on (Comm. 147a, 1915) the somewhat smaller value 315 was found between 14° and 90° abs.

As at 20° C σ is found $= 0,730 \cdot 10^{-12}$ (see Chapter V of the previous paper), the value of σ will only be $\underline{0,681 \cdot 10^{-12}}$ at $T = 0$, again not very different. Hence we have:

$$\begin{array}{l|l} T=0 \text{ (abs.)} & \theta=331; \sigma=0,68 \cdot 10^{-12} \\ T=293 \text{ (20}^{\circ} \text{ C.)} & \theta=321; \sigma=0,73 \cdot 10^{-12}. \end{array}$$

The differences are so small, that it may safely be said that (p supposed $= 0$) the values of θ and σ practically vary little between the absolute zero and the ordinary temperatures.

And as the values of the coefficients of expansion have been given by (see § 4)

$$\alpha = \left(\frac{dp}{dt} \right)_v \times \sigma,$$

the values of α ($\sigma = \text{constant}$) will about vary with those of $\left(\frac{dp}{dt} \right)_v$; i.e. the values of α at ordinary temperatures will be to those at very low temperatures as $\frac{R}{v-b} \sigma$ to $\frac{4PT^3}{v-b} \sigma$, hence (the values of $v-b$ being resp. $= 1,186$ and $1,138$) as $(R : 4PT^3) : 1,042 \times 1,072$ (see above).

We have accordingly:

$$\alpha = (20^{\circ} \text{ C.}) : \alpha (20^{\circ} \text{ C. abs.}) = 83,17 \cdot 10^6 : (471,9 \times 20^3) \times 1,029 = 22,7.$$

In § 4 we found about this ratio $51 : 2,261 = 22,6$.

In a concluding article we will briefly discuss the calculation of the *heat of melting* and the *heat of evaporation* for solid substances, and also the derivation of the equation of the vapour pressure at higher and lower temperatures. Besides, the dimensions of the closed paths round the positions of equilibrium will be treated; and then there only remains to test the equation of state drawn up by us by all other metals of which BRIDGMAN has determined the coefficients of compressibility and their coefficients of pressure and temperature with so great accuracy. By the aid of these two papers this can now easily be done, and may, if need be, be left to others.

N.B. It is self-evident, that in all that precedes there is only question of solid substances, which with regard to the three principal directions show identical properties. Otherwise the quantities b_g , b_{00} , and λ will have different values in the said directions, and properly speaking there are three equations of state, or, as it may also be expressed, one mean equation of state.

Tavel sur Clarens, Suisse, Dec. 1925.

Botany. — "On the Periodical Movements of the Primary leaves of *Canavalia ensiformis*. D. C." By G. BROUWER Sc. D. (Communicated by Prof. G. VAN ITERSON Jr.)

(Communicated at the meeting of December 19, 1925).

The present investigations derive their origin from a number of preliminary tests carried out in the Botanical Laboratory of Utrecht. But my experiments had to be put a stop to through circumstances that rendered further researches impossible there. With the consent of Prof. F. A. F. C. WENT Sc. D. the following experiments were, therefore, conducted in the Laboratory for Technical Botany of Delft. Prof. G. VAN ITERSON JR. Sc. D. not only granted me free use of a large dark room, part of a greenhouse, and all the instruments required, but also assisted me by word and deed, for which I still feel greatly indebted to him.

It is a matter of common knowledge that the leaves of many plants change their position at night. In *Phaseolus*-species, e.g., the leaves are vertical by night and horizontal by day. The leaflets of the compound leaf of many *Leguminosae* fold themselves together at night. Originally it was believed that the alternation of night and day brought about these "sleep-positions"; hence the name "Nyctinasty". This term is still generally used without any meaning being attached to the word "nasty".

The first investigators that occupied themselves with the problem of nyctinasty, determined some times a day the angle made by the leaf-blade or the leaf-stalk with the vertical. The points thus obtained they joined by lines, thus tracing a curve, that represented the daily movement of the leaf.

In 1907, however, W. PFEFFER²⁾ was the first to use the self-recording method. He attaches the leafblade by a silk thread to a glass rodlet leaning against the smoked drum of a kymograph. When the leaf lowers, the pointer rises and conversely. This produces a curve, registering the exact position of the blade from hour to hour. His experiments with *Mimosa*, *Acacia*, *Albizzia* and *Phaseolus* induced him to form the following conception of sleep-movements. They are photonastic reactions, originating through the alternation of day and night. In constant light or constant darkness, therefore, a cessation of the movements occurs ("Licht-, and Dunkelstarre"). Beyond this the smaller daily oscillations occur, consisting in slight up- and down movements of the blade. These movements are held to be of an autonomous nature and to be owing to internal factors.

In 1905⁶⁾ and 1907⁷⁾ SEMON had tried to explain the periodical leaf-movements by means of his "Mneme"-theory; he considers the nyctinastic

movements to be perfectly autonomous. So SEMON and PFEFFER hold quite different opinions in this respect.

In 1910, however, R. STOPPEL⁸⁾ notes that *Calendula*-flowers keep performing the diurnal movements also in constant light, while she discovers in 1919⁹⁾ that *Phaseolus*-plants reared in the dark, perform movements in a daily rhythm.

Furthermore, in 1911³⁾ and 1915⁴⁾ PFEFFER established that *Phaseolus*-leaves retain their normal moving-capacity also in constant light, provided that the blade-articulation (i.e. the transition from leaf-stalk to leaf-blade) be wrapped up in blackened cottonwool. PFEFFER also concludes from these facts, that there are plants which can perform autonomous movements in a daily rhythm; in this process, however, light can be a prime regulator, for he has easily succeeded in inducing another period by illuminating by night and applying darkness by day i.e. by giving from 8 to 18 hours light and from 8 to 18 hours darkness.

A totally different explanation of nyctinasty was brought forward by R. STOPPEL¹⁰⁾ in 1916. She placed some plants isolated or made use of positively or negatively charged cages, and of emanation-containing substances, and came to the conclusion that the periodical changes in the conducting power of the atmosphere must be looked upon as the direct cause of sleep-movements.

In 1922 SCHWEIDLER and SPERLICH⁵⁾ put some of her experiments to the test, but could not confirm her results. Accordingly they believe that the sleep-movements have been established by heredity.

In 1912 HANS CREMER¹⁾ repeated the greater part of STOPPEL's experiments. Again the result was negative, so that he concludes that electricity cannot be the cause of the sleep-movements. The results achieved by his experiments in a disused shaft are very remarkable. Etiolated *Phaseolus*-plants which had a distinct diurnal period in the dark room of the laboratory, were removed to this shaft and kept under precisely the same conditions: the movements ceased. When conversely motionless plants were removed from the shaft to the dark room, the movements returned.

CREMER rightly concludes: "Es handelt sich um einen noch unbekannten Faktor."

It is evident from this brief summary of the literature that the essential problem is whether nyctinasty is autonomous or aitionomous, and if aitionomous, what is the external factor (or the complex of external factors) that generates the daily movements of the leaves?

In the beginning I worked with *Phaseolus*. Afterwards I found a very suitable object in *Canavalia ensiformis* D. C., with which all the following experiments were made. The seedlings of this species acquire large, very strong leaves which stand quite horizontal by day and fall so low at night that they pass beyond the vertical and lean against the stem. Also in constant darkness they remain perfectly green up to a fortnight sometimes

and perform the daily sleep-movements. Even right in the darkest winter-months robust plants develop from the seed. At first I procured this seed

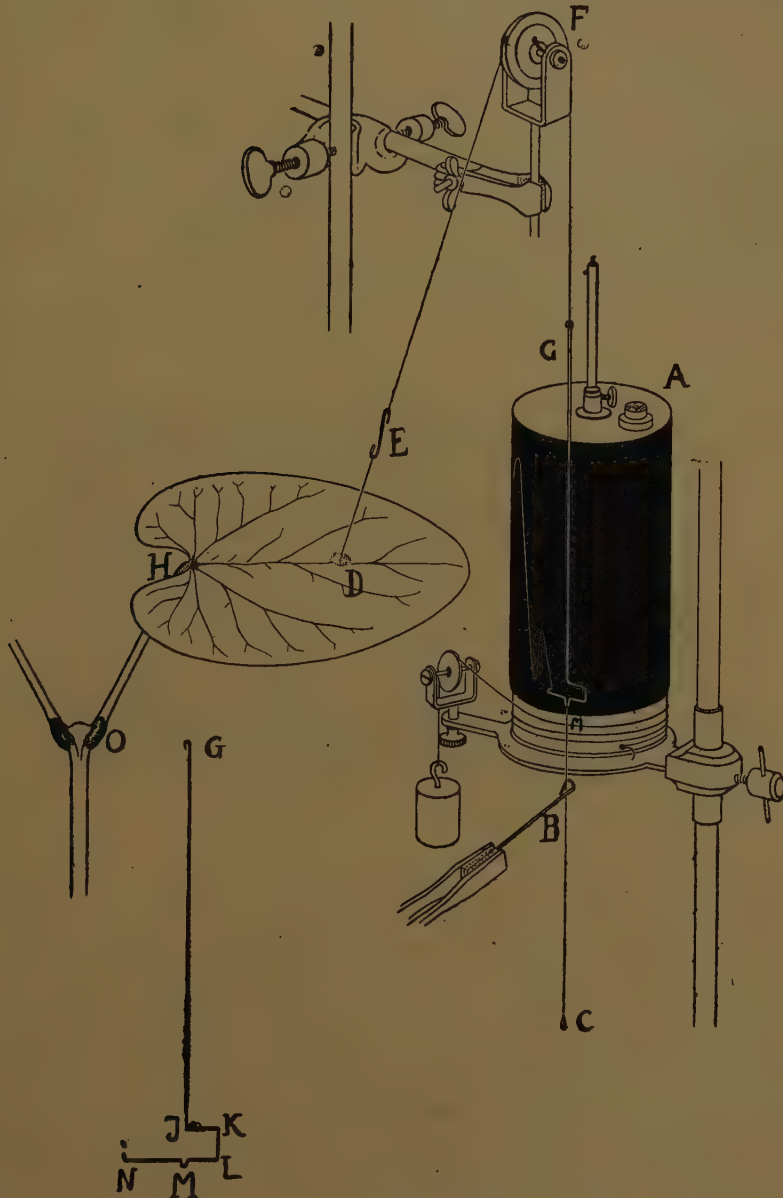


Fig. 1.

from different botanical gardens in Europe, but since Prof. Dr. STAHEL of Paramaribo sent me a large collection of West-Indian seed, I used them in my further experiments, since from them I could raise the best developed plants.

Rather many objections to PFEFFER's recording method may be raised,

so that I applied another method, of which I present the following brief description :

A silk thread DEG runs from the leaf-blade over a small nickel pulley F. At the end of this thread is suspended a glass pointer GM. Its form is shown in the figure. The plant is placed as favourably as possible, and the kymograph is brought in tangential position with the pointer. In order to obtain a clear curve it is desirable to twist the pointer slightly. At the lower end of the pointer a little weight C is suspended, that serves to keep the pointer and the thread well taut. In order to check incidental oscillations of the weight the thread MC runs through a glass cyclet B. To get proper curves with this pointer it is first of all required that all its bends are vertical to each other, and that they all lie in the same plane (except the extreme point).

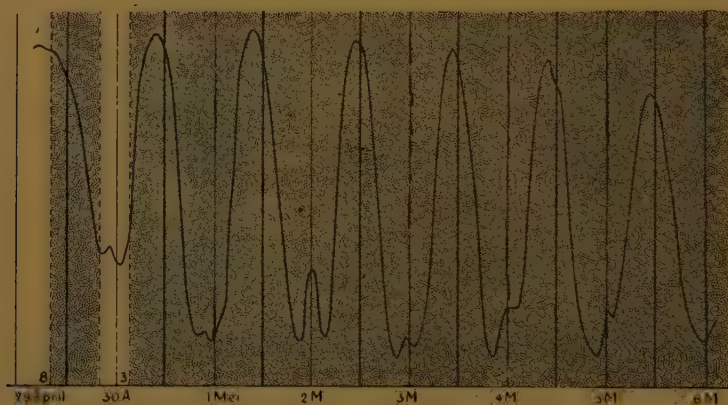


Fig. 3.

When the leaf descends, the pointer of course goes up ; when the leaf rises, the pointer goes down. The apex of the curve is the "night-position", the base of it is the "day-position" of the leaf.

Every day a given hour was indicated by a small mark on the curve. By rotating the drum quickly a horizontal line is produced, where the time-lines (midday : thin line with datum ; midnight : thick line) are traced vertically. The distance from the thread to the blade-articulation was 7.5 cm. (HD).

The greenhouse in which some of my experiments were carried out was large and spacious, and there was always plenty of light. The experiments in artificial light I made in the dark room, where temperature and humidity were maintained constant. The illumination was provided by two "sunlight"-lamps of PHILIPS each of 1000 c.p. These lamps were placed in large bells, cooled by running water. The light fell from above on the leaves.

In the years spent on this investigation I have made a great many experiments, some of which I will report here. Most of them I made with

three or four plants at a time, which enhances the reliability of the results, while some experiments were performed more than once.

The curve traced by a *Canavalia*-leaf in the experimenting greenhouse under normal conditions I call the "Normal-curve". Now, what strikes us is that the normal-curves of many plants, irrespective of the origin of the seed, display many similarities. Even the movements of the leaves of the Surinam plants were in the main the same as those of the plants derived from the seed of European Botanical gardens. Neither was any difference noticeable between the curves drawn in winter and those drawn in mid-summer. When the plants in the dark room were exposed to a normal period of light and darkness by inducing darkness at 8 in the evening and light at 8 o'clock the next morning, the curves thus obtained were broadly speaking again equal to the normal-curves. This surely suggests that most probably the same external factor produces the homomorphous curves of these plants drawn from such different sources.

In fig. 2 we see the normal-curve of a plant that was for seven days in the

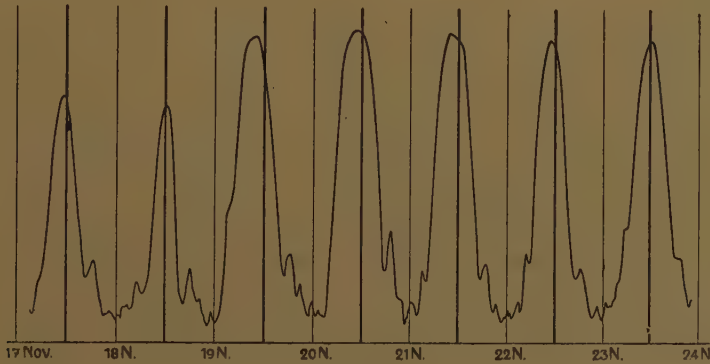


Fig. 2.

greenhouse. It is evident from this curve that the lowest position always falls about midnight, the highest between 6 o'clock a.m. and 2 o'clock p.m., in the day position we find the small oscillations.

PFEFFER looks upon them as autonomous movements, but I presume to have found an other interpretation on the basis of the following experiments.

When we cut away the upper side of the articulation of the leaf-blade, the leaf, to be sure, will continue the daily movements, but with this difference that it does not descend deep in the evening, it only performs rather great movements round the horizontal in a daily period. When we cut away the under side, the leaf will go down till the point of the blade comes in contact with the stem. In this position it persists for weeks. This may be interpreted by assuming that the upper side of the articulation has rather a large but a *constant* turgor, while on the contrary the under-side is very sensitive to an unknown external stimulus, which alters the tension in this half in the early morning and in the afternoon, whereby the leaf-blade

rises or lowers itself. So when the upper side is cut away, the leaf will sink far less deep, but its movements will continue. When the under side is removed the upper side will press the blade down and keep it in that position.

Now, when the leaf stands in the day-position, the static moment of the blade relative to the articulation will be greatest, while the tensions in the upper and under side of the articulation will be equal. But as soon as, in consequence of the small changes in the metabolism (respiration, assimilation, evaporation), the turgor in the under side diminishes at all, the leaf will be pressed down slightly. This, then, explains that the small oscillations always occur in the day-position. It is very easy to prolong the period by giving 24 hours light and 24 hours darkness. The sleep-movements then assume a rhythm of 24 hours whereby the highest position of the leaf falls exactly in the dark period, the lowest in the light period. Still, the small oscillations occur in the day-position, (i.e. in the dark).

When we cut off the leaves and put them in bottles filled with water, the sleep-movements still persist firmly for about 10 days. When, however, the articulation of the petiole (on the junction of stem and central vein) is present, the leaves will be withered after one or two days.

I have gone further and have removed from the cut leaves all the parenchyma, so that only the leaf-stem, the articulation, and the central vein (± 15 cm) were left. This I shall designate by the term "Strip". Now, suchlike strips keep up fine, distinct, nyctinastic movements for days. Especially in the dark room their movement remains normal for a week, above all when they are kept standing in the dark (fig. 3). From these experiments it is very clear that the sleep-movements are in a high degree independent of the life-functions of the other parts of the plant, such as root-pressure, assimilation, evaporation, and respiration. Apparently the leaf-blade is not the precipient part, and the articulation is the active part; it looks completely as if the articulation performs both functions.

When I reared a large number of plants from the seed under perfectly constant conditions in constant light, it appeared that they still performed the daily sleep-movements, although they had never been known to have had any contact with a periodically changing factor (except of course the seed during its development in the fruit). The movements were, however, not very regular; now there were high apices, then again low ones; but freakish though the movement-picture may sometimes have been, it still revealed many striking similarities in control-plants that were used at the same time. At it happens, when I exposed plants from the greenhouse, in the dark room to constant light or constant darkness, the sleep-movements continued undiminished. With cut leaves and strips (Fig. 3) the results were the same. It is peculiar though, that in constant darkness the amplitude of the movements was larger and much more regular than in the light. Sometimes it happened that without any (known) cause the period reverted, so that the leaves assumed the day-position in the evening,

and in the morning the sleep-position; and after some days the rhythm was normal again unexpectedly.

PFEFFER and STOPPEL and others found that in *Phaseolus* a rigidity set in in constant light and in constant darkness. ("Dunkel- und Lichtstarre"). But when they envelop the articulation of the leaf-blade in blackened cottonwool, the sleep-movements continue in constant light. When studying the curves constructed by PFEFFER, I noted that in *Phaseolus* similar reversions and shiftings of the period also occur in the light, although he says nothing about it. In constant darkness *Phaseolus* dies in a couple of days; it appears, therefore, that "Dunkelstarre" is a phenomenon of decay. Only after about ten days do the robust *Canavalia*-plants begin to suffer from the metabolic anomalies caused by constant darkness. So it is probably for that reason that no rigidity appears in those leaves. Light seems to be deleterious to the articulations, which renders their movements less regular.

As stated before, there is a reversion of the period of the sleep-movements within 24 hours, when illumination takes place by night and darkness is kept up in the daytime. A number of experiments proved that this reversion proceeds with the same rapidity when, after some days of a normal, periodical illumination the light is not put out in the evening, and when the light is not turned on in the morning during some days. In the first case the reversion is brought on by 12 hours' extra light, in the second case by 12 hours' extra darkness. When the reverted period had then been induced after some days, the plants were placed in constant darkness. Now it is noteworthy that after three or four days the night-apices shifted gradually, so that after that time the leaves performed again their sleep-movements in the normal rhythm.

However, when, after having given the reverted period after the same number of days, I kept the leaves in constant light, I saw to my surprise that within 24 hours the normal tempo of movement was resumed. This is expressed by the curve fig. 4. To really grasp what strikes us in this reaction the following points should be compared.

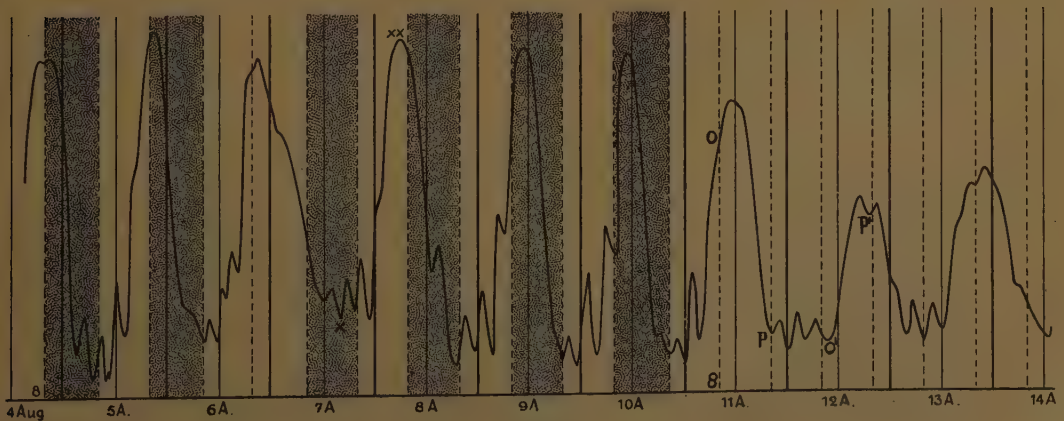


Fig. 4.

11 Aug. 8 o'cl. a.m. (O), with 12 Aug. 8 o'cl. a.m. (O') and
11 Aug. 8 o'cl. p.m. (P), with 12 Aug. 8 o'cl. p.m. (P').

In order to account for these phenomena we must assume that light largely increases the sensitiveness of the articulations for an unknown factor. But the same influence of light must be held responsible for the fact that after some days of constant light the period becomes irregular again. Broadly speaking we can say, therefore, that in constant darkness the leaves move much more regularly than in constant light. *Phaseolus* tolerates unintermittent light far less than *Canavalia* does; it prevents the articulations from reacting unless they are guarded by black cottonwool.

In resuming we can set up the following working hypothesis:

There is in the atmosphere a factor (or a complex of factors) that changes periodically every day (perhaps in consequence of the succession of day and night). The changes are brought about in organs susceptible to the influence of the factor, in casu the articulations, by which the leaf-blade or the leaf-stem performs the so called sleep-movements. This factor also penetrates into closed spaces; it is consequently the cause that, in constant light or constant darkness, in *Canavalia* and in *Phaseolus* (under certain circumstances) the movements do not cease. Light largely enhances the sensitiveness of the articulations to this factor, which makes it possible to revert the daily period, or to impart to it another rhythm (24:24). This is why leaves that have a reverted period will resume the normal movements in constant light directly after this, but in constant darkness only after some days. Plants reared in constant light will on this account have a daily period, which, however, becomes irregular through the constant effect of in-flowing light. Now it is obvious also, that it does not matter for the amplitude of the normal curve whether the plant is placed in the greenhouse or in the dark room with artificial, periodical illumination; the amount of light, therefore, is immaterial. (PFEFFER 4 lamps of 40 c.p.; SEMON lamps of 10 c.p. and the present writer 2 lamps of 1000 c.p.).

The insignificant oscillations in the day-position result from the horizontal position of the leaf-blade, for in that position small changes in the turgor of the articulations will be of greater influence than with a vertical position of the blade.

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December 1925.

Geology. — "*On the Occurrence of the Danau-formation in Martapura (S.-E. Borneo).*" By L. RUTTEN.

(Communicated at the meeting of Jan. 30, 1926).

When reading the petrographical description by J. RETGERS ¹⁾ of the rocks, collected by J. HOOZE ²⁾ in his prolonged exploration in Martapura, we are struck by the details reported concerning the rocks of the "Waringin- and Alino clayrock-formation", which seem to indicate that there are among them true radiolarites. A priori it would be quite conceivable if RETGERS and HOOZE had not recognized radiolarites as such, for their publications date from 1891 and 1893, while radiolarites-containing deposits in the Archipelago were not taken an interest in before 1897, when HINDE described a radiolarite from Billiton ³⁾, and above all when in 1900 MOLENGRAAFF's work on Borneo ⁴⁾ appeared.

When more than a twelvemonth ago I found the above indications in RETGERS' descriptions, I remembered having seen years ago in Bandjirmasin a siliceous gravel intended for paving a road, which contained many red cherts that, when looked at, bear great resemblance to the radiolarites of the Danau-formation and was derived from Martapura. I asked the pro-tem Director of the Mining Department of the Neth. East Indies Dr. J. K. VAN GELDER to be so kind as to send me a number of splinters of the rocks from HOOZE's collection. These I examined in the past month. I feel glad to have an opportunity now to tender my thanks to Dr. VAN GELDER for his kind assistance. Before reporting the result of my examination I have to refer to a few items in the recent literature.

Once already the possibility has been surmised that the Alino- and Waringin-clayrocks bear some resemblance to the Danau-formation in W.-Borneo. N. WING EASTON ⁵⁾ wrote when he compared the Pretertiary of W.-Borneo with that of E.-Borneo :

"Also in the district of Martapura this Danau-formation seems to exist, notably in the sediments mentioned by HOOZE, who called them „Waringin and Alino-clayrocks". Those sediments crop out in small massifs in a region with prevailing cretaceous sediments which are younger than the "clayrocks". Here also we meet again with that typical siliceous slate and quartzite" (l. c. p. 187, 188).

¹⁾ J. W. RETGERS, Jaarb. Mijnwezen, 1891. Wetenschappelijk gedeelte.

²⁾ J. A. HOOZE, Jaarb. Mijnwezen, 1893.

³⁾ G. J. HINDE, Jaarb. Mijnwezen, 1897, p. 223—227.

⁴⁾ G. A. F. MOLENGRAAFF, Borneo Expeditie, 1900.

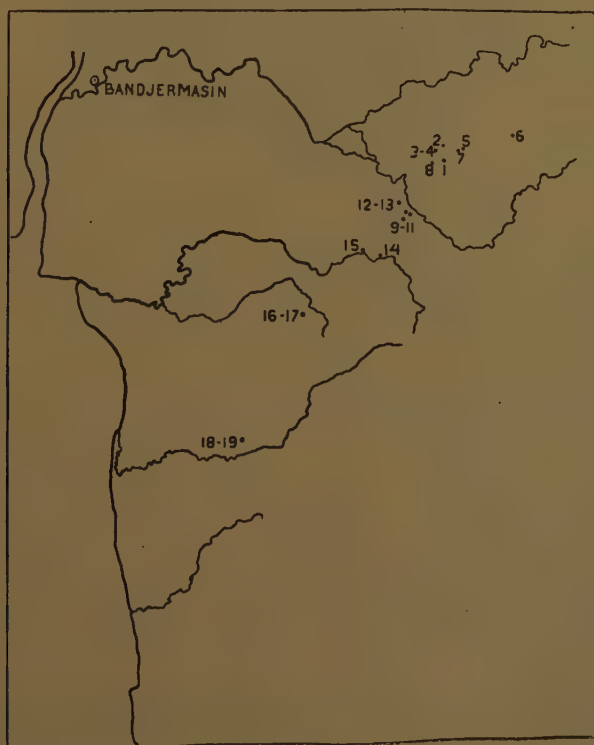
⁵⁾ N. WING EASTON, Geol. Mijnb. Genootschap Nederland en Koloniën. Geol. Sectie Verslagen der vergaderingen 1. 1914, p. 179—189.

EASTON's view, which is apparently based not on his own investigation ¹⁾ of the rocks, but on HOOZE's communications, has also been adopted by VAN ES ²⁾ in 1919. On the other hand not a trace of it is discernable in the recent publications on S.-E.-Borneo by KROL ³⁾. On the contrary, KROL's conception of the Alino-clayrocks is quite another one. He takes them to be cenomanian sandstones and clayrocks built up mainly of detrital, prophyritic material, which has been metamorphosed by contact with cenomanian peridotites and other intrusive rocks. A few quotations may serve to elucidate this :

"The Alino- and Waringin layers.... I take to be layers of cenomanian age, which were metamorphosed intensively by contact with the peridotites" (p. 312, 313).

"Conglomerates and sandstones (of the Cenomanian) are the direct detritus of the eruptiva, that have formed the original mainland and may most often be derived from the (red or brown) porphyrites" (p. 314).

This conception is but sparingly substantiated on HOOZE's map, on which we see the "Alino- and Waringin-clayrocks" marked on the north-western slope of the Meratus-mountains over a distance of 55 km. — though with some local breaks — while only over half this distance they



1) See however the "addendum" at the end.

2) L. VAN ES, Jaarb. Mijnw. 1917. Verhandelingen 2. 1919. p. 127—128.

3) L. KROL, Jaarb. Mijnw. 1918. Verhandelingen 1. 1920. p. 281—367.

lie in contact with a long peridotite band; particularly in the north-eastern part of the "clayrocks" they are removed about 5 km. from the peridotite-margin.

Now the inspection of the rocksplinters from India has made out that among the rocks classed under the "Alino- and Waringin-clayrock", Radiolaria-cherts unquestionably occur, that resemble in every respect the Radiolarites from the Danau-formation in W.-Borneo. Some rocks contain Radiolaria with still beautifully preserved structures (Fig. 1); in

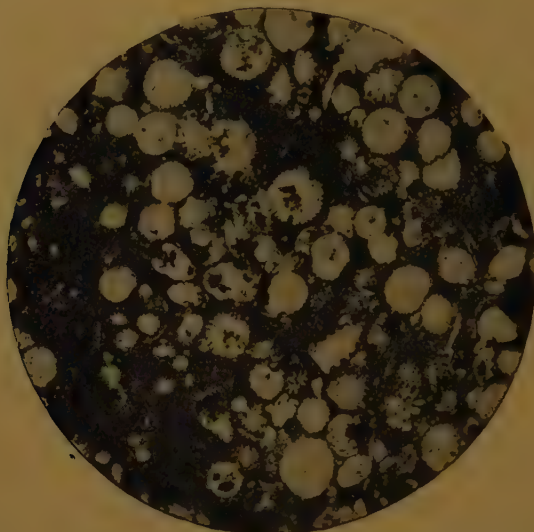


Fig. 1. Radiolarite: Mungu Tiang Hadji besar. HOOZE 334, D. 10121. Magnified $\times 50$.

others the structures are for the greater part lost — chiefly through weathering —; but still here and there unmistakable remains of Radiolaria can be identified; others again have been entirely recrystallized, so that the rocks are "siliceous slates" pure and simple, although in all probability we have to do here with altered Radiolarites. Various splinters originated from silicified tuffs, and in one case remains of Radiolaria were still recognized in such a tuff, which suggests that, just as in W.-Borneo, the period of the formation of the Radiolarites was at the same time a period of volcanic activity. The complete description of the rocksplinters examined is given in the subjoined "Appendix"; out of 19 of the examined rocks no less than 12 appeared to contain recognizable Radiolaria from localities distributed over almost the whole area of the Alino- and Waringin-clayrocks.

It imports us to know that it becomes more and more apparent that a great resemblance exists between the geology of Martapura and that of the Central Kapuwas territory: Schists, Danau-formation, Cenomanian with Orbitolina and Intrusiva appear to occur equally in both territories. Strange to say, KROL considers the Intrusiva in Martapura to be intra-

cenomanian, although in Western-Central-Borneo their precenomanian age has been established.

APPENDIX.

Description of a number of rock-samples from the
„Alino- and Waringin-clayrocks" in Martapura:

No. 1. (HOOZE IX, 289. See HOOZE l. c. p. 147: Compact rock from uppermost part of Pantjuran Hill. D. 10118). A red, slightly porous, steaky rock; the microscopical section reddish brown through diffused limonite, consisting of an extremely fine silicic-acid mass, with many circular holes reminding one at once of Radiolaria. In one case unmistakable wall-structure, in many other cases this structure was vague. *Weathered Radiolarite.*

No. 2. (HOOZE IX, 286. See HOOZE l. c. p. 147; G. Kaju Tawon D. 10124). Greyish-pink, finely porous, very hard rock which contains numberless circular to ellipsoidal hollows whose wall is for the greater part structureless; radiolarian wall-structures are still distinctly visible at several places. *Weathered Radiolarite.*

No. 3. (HOOZE IX, 287. See HOOZE l. c. p. 147. G. Plappa. D. 10125). An extremely fine-grained, whitish-yellow, siliceous rock with few, partly altered Radiolaria some of which present structure. *Weathered Radiolarite.*

No. 4. (HOOZE IX, 228. See HOOZE l. c. p. 147. Base G. Plappa. D. 10126). Very finely granular, siliceous rock with — partly weathered — remains of Radiolaria. *Weathered Radiolarite.*

No. 5. (HOOZE 290. See HOOZE l. c. p. 147. G. Linu D. 10127). Violet, very fine-grained, markedly porous rock, certainly identical with the preceding rock. The numberless hollows, corresponding with earlier Radiolaria have, however, become quite structureless. *Weathered Radiolarite.*

No. 6. (HOOZE 217. See RETGERS l. c. p. 40: S. Takuti, 4 km. east of Bt. Kemin-ting, D. 10130). On HOOZE's map no Alino-clayrock has been marked in this locality. It is in fact a volcanic tuff, with fresh, sharp-edged plagioclases.

No. 7. (HOOZE 220. See RETGERS l. c. p. 40: S. Laba, tributary S. Pangaringan. D. 10131). Is a tuffogenic, very fine-grained rock, containing numerous, though not very well preserved rests of Radiolaria. This *Radiolaria-bearing tuff* goes to show that at the time of the formation of Radiolarian deposits volcanic activity took place.

No. 8. (HOOZE 295. See RETGERS l. c. p. 41: S. Limau gulung near G. Tarung kili. D. 10128). Very finely granular rock with flaky, accumulated limonite, with numerous spherical corpuscles, some of which still display lattice-wall structures. *Weathered Radiolite.*

No. 9. (HOOZE IV. 53. See RETGERS l. c. p. 113: Mungu Tanggiling, S-base. D. 10132). White spotted, pink finely porous rock, completely silicified, perhaps a *Silicified Tuff* ? ?

No. 10. (HOOZE IV. 54 See RETGERS l. c. p. 114: Mungu Batu Kutjut East, circa 500 m. N. W. of the preceding rock. D. 10122). Very fine-grained, brownish-red, siliceous rock, locally completely recrystallized, without a trace of fossils. *Siliceous slate.*

No. 11. (HOOZE IV. 68. See RETGERS l. c. p. 114: Top Bt. Tunggul, 2 km. W.S.W. of the preceding. D. 10133). Weathered, pinkish-white-spotted rock, siliceous, markedly altered, possibly (but this is very uncertain) with remains of Radiolaria. *Siliceous slate.*

No. 12. (HOOZE IV 28. See RETGERS l. c. p. 112: Mungu Batu hitam laki. D. 10134). Spotted, brown, siliceous rock, markedly recrystallized, possibly but not certainly, with Radiolaria. *Siliceous slate.*

No. 13. (HOOZE IV 13. See RETGERS l. c. p. 112: Mungu Batu hitam parampuan. D. 10123). Markedly recrystallized, reddish-brown rock, without determinable organic remains. *Siliceous slate*.

No. 14. (HOOZE IV. 114. See RETGERS l. c. p. 114: Padang, SE, of Sign. Pematton. D. 10137). No Alino-clayrock has been marked here on HOOZE's map. Completely limonitised rock, probably with remains of numerous Radiolaria? *Weathered Radiolarite*.

No. 15. (HOOZE IV. 103. See RETGERS l. c. p. 114: Mungu Sekumpang ketjil, W. of Sign. Pematton. D. 10135). Possibly a *silicified tuff*, anyhow without recognizable organic remains.

No. 16. (HOOZE IV. 184. See RETGERS l. c. p. 115: Sign. Padang Kalang Badak. D. 10119). Brecciated, siliceous, fine-grained rock with numerous Radiolaria, which sometimes still display fine structures and always typical forms. *Brecciated Radiolarite*.

No. 17. (HOOZE IV. 185. See RETGERS l. c. p. 115: Sign. Padang Kalang Badak. D. 10120). Resembles No. 16, is a brecciated, reddish brown, siliceous rock, in which, however, occur only few but unmistakable Radiolaria. *Brecciated siliceous slate with Radiolaria*.

No. 18. (HOOZE IV 335. See RETGERS l. c. p. 188: Mungu Tiang Hadji besar. D. 10136). Reddish brown, siliceous rock with numerous spherules, some of which have decidedly the structure of Radiolaria. *Radiolarite*.

No. 19. (HOOZE 334. See RETGERS l. c. p. 187: Mungu Tiang Hadji Besar. D. 10121). Of all rocks examined this is the most typical *Radiolarite*, reddish-brown, with numberless Radiolaria microscopically well preserved for the greater part. The microphoto in Fig. 1 has been taken from the section of this rock.

N.B. The numbers *before* the rocks are the same as those on the accompanying map of the localities. The numbers preceded by D. refer to the collections of microscopical sections in the Geological Institute of the Utrecht University.

Utrecht, January 1926.

Addendum. When the Dutch text of this note had appeared, Mr. WING EASTON informed me, that he has already seen radiolarian structures in HOOZE's rocks as early as about 1900. However, he never published his observations, as he only began to have real interest for S.-E. Borneo much later, when it was impossible for him to check his recollections by renewed microscopical study.

Physics. — "*The Crystal Structure of Red Mercuric Iodide.*" By J. M. BIJVOET, A. CLAASSEN and A. KARSSSEN. (Communicated by Prof. W. H. KEESOM).

(Communicated at the meeting of January 30, 1926).

1. This investigation was taken up in view of the allotropic behaviour of HgI_2 ¹⁾.

We intend to investigate at a later date its yellow rhombic modification and the isomorphous HgBr_2 .

According to GROTH ²⁾ red mercuric iodide crystallizes in the ditetragonal-bipyramidal class of the tetragonal system, with an axial ratio $a : c = 1 : 2,008$.

The crystals for our *X*-ray analysis were obtained by slow crystallisation from metyliodide solution and formed dark red quadratic prisms. They possess a very perfect cleavage parallel to the basal plane.

For the rotation diagrams crystals of 1 or 2 mm. diameter were used.

2. *Apparatus.* This has been described by J. M. BIJVOET and A. KARSSSEN ³⁾. Radius of the camera 2,47 cm. During the exposure the crystals were rotated by clockwork. The exposures lasted about 30 hours with a mean current of 6 milliamps.

3. *Determination of the elementary-cell.*

The dimensions of the unit cell can be determined by means of rotation diagrams, in which the crystal is rotated about some crystallographic axis. The *X*-ray period ("Identitätsperiode") *I* along this axis can then be found from the distance of the zone to the equator, according

to the formula of POLANYI ⁴⁾: $I = \frac{n \lambda}{\cos \mu}$. In this formula *n* = zone-number;

λ = wavelength and μ the angle between zone and equator as defined by $\text{tg } (90 - \mu) = \frac{l}{R}$ with *R* = radius of the camera.

Combining these two formulae we get:

$$I = n \lambda \sqrt{1 + \frac{R^2}{l^2}}.$$

The following table I gives the measured *X*-ray period of various crystallographic axes, as calculated by the above formula. Each value is an average from several films.

¹⁾ A. SMITS, *The Theory of Allotropy*. London, 1922.

²⁾ P. GROTH, *Chemische Krystallographie* I, pag. 218.

³⁾ J. M. BIJVOET—A. KARSSSEN. *Rec. Trav. Chim.* **42**, 589 (1923), **43**, 680 (1924).

⁴⁾ M. POLANYI, *Zeitschr. f. Phys.* **7**, 170 (1921). **9**, 123 (1922). **10**, 44 (1922).

TABLE I. X-RAY PERIODS.

Rotation-diagram about [001]								
$\lambda = 1,539 \text{ \AA} (\text{CuK}\alpha)$			$\lambda = 1,936 \text{ \AA} (\text{FeK}\alpha)$			$\lambda = 2,286 \text{ \AA} (\text{CrK}\alpha)$		
n	$2l$ in cm.	$I_{[001]}$	n	$2l$	$I_{[001]}$	n	$2l$	$I_{[001]}$
1	0.62	12.38 \AA	1	0.78	12.38 \AA	1	0.93	12.48 \AA
2	1.26	12.48	2	1.61	12.43	2	1.93	12.51
3	1.98	12.42	Average 12.41 \AA			3	3.27	12.40
4	2.81	12.45				Average 12.46 \AA		
5	3.90	12.42						
Average 12.43 \AA								

Rotation-diagram about [100]			Rotation-diagram about [110]		
$\lambda = 2,286 \text{ \AA}$			$\lambda = 2,286 \text{ \AA}$		
n	$2l$	$I_{[100]}$	n	$2l$	$I_{[110]}$
1	1.96	6.20 \AA	1	3.06	4.35 \AA

Rotation-diagram about [101]			Rotation-diagram about [111]		
$\lambda = 2,286 \text{ \AA}$			$\lambda = 2,286 \text{ \AA}$		
n	$2l$	$I_{[101]}$	n	$2l$	$I_{[111]}$
1	0.83	13.81 \AA	1	0.75	15.25 \AA
2	1.73	13.84	2	1.57	15.12
Average 13.83 \AA			Average 15.19 \AA		

From the rotation diagrams about [100] and [001] there follows for the dimensions of the unit cell in these directions 6.20 \AA and 12.43 \AA , respectively. This gives an axial ratio agreeing very well with the one determined goniometrically (§ 1).

The [110] period is calculated as $6.20 \sqrt{2} \text{ \AA} = 8.76 \text{ \AA}$.

In table I we found $I_{(110)} = 4.35 \text{ \AA}$, hence the [110] period is halved. For the [101] and [111] directions we calculate from the cell dimensions 13.89 \AA and 15.22 \AA respectively; the X-ray periods found (see table I) indicate that these directions are not halved.

The literature gives for the density of red HgI_2 6.28 to 6.30.¹⁾

¹⁾ P. GROTH. Chem. Krystall. 1, pag. 218. VAN NEST, Z. f. Krystall. 47 265 (1910.)

From this the number of molecules per unit cell appears to be 4.

Starting from 4 molecules per cell and the above found cell-dimensions we calculate the density as 6.28.

This unit cell however is not the smallest one possible. Indeed, the smallest *X*-ray period in the basal plane being equal to 4.38 Å, by turning the system of coordinates about the four-fold axis through 45°, a new elementary cell can be assumed with dimensions 12.43 Å × (4.38 Å)². This cell contains only two molecules.

The values of $10^3 \sin^2 \frac{\vartheta}{2}$ must fulfil a quadratic equation in the Millerian indices, which for the tetragonal system reads:

$$\sin^2 \frac{\vartheta}{2} = \frac{\lambda^2}{4a^2}(h^2 + k^2) + \frac{\lambda^2}{4c^2}l^2.$$

With the above found dimensions of the unit cell, viz.:

$a = 4.38$ Å; $c = 12.43$ Å we get the following formulae for $10^3 \sin^2 \frac{\vartheta}{2}$

$$10^3 \sin^2 \frac{\vartheta}{2} = 30.9(h^2 + k^2) + 3.83 l^2 \text{ for } \text{CuK}\alpha$$

$$10^3 \sin^2 \frac{\vartheta}{2} = 68.0(h^2 + k^2) + 8.45 l^2 \text{ for } \text{CrK}\alpha.$$

From these equations indices have been assigned to the reflections on the rotation-diagrams about various axes. The excellent agreement between calculated and observed values brings out the correct choice of the unit cell.

The indices referring to the smallest cell (*h k l*) can be deduced from those relating to the crystallographic cell (*H K L*) by means of the transformation:

$$h = \frac{1}{2}(H + K), k = \frac{1}{2}(H - K), l = L.$$

When the observed and calculated values of sine-squares of the rotation diagrams are compared, it appears that the observed values are always 8 to 10 units larger than the calculated ones; this is in good agreement with the corrections to be expected for the thickness of the crystals (1 to 2 mm.). The factors in the formulae given above agree well with the powder films corrected for the thickness of the rod.

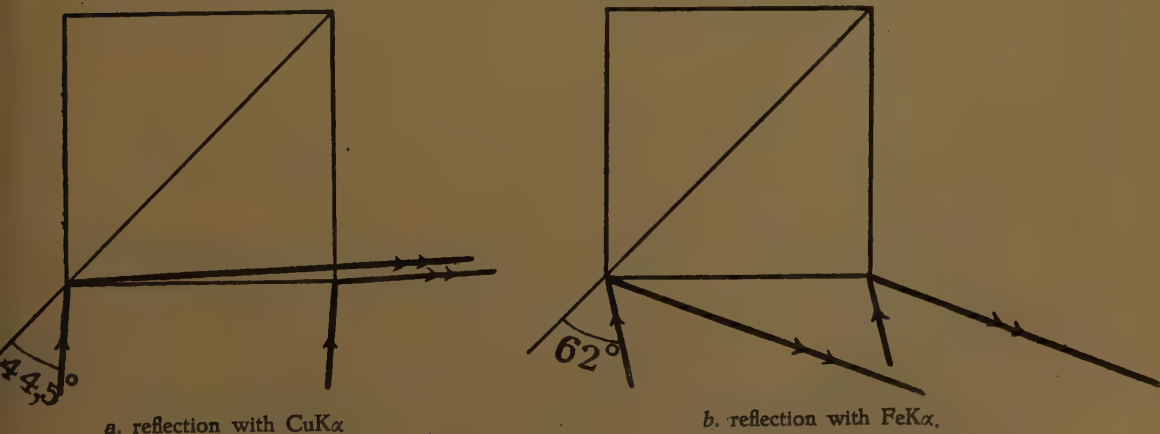


Fig. 1.

TABLE II. ROTATION-DIAGRAM ABOUT [001].

$\lambda = 1,539 \text{ \AA}$	Distance in cm.	Intens.	$10^3 \sin^2 \vartheta/2$ observed	$10^3 \sin^2 \vartheta/2$ calculated	hkl	$\lambda = 1,934 \text{ \AA}$	Distance	Intens.	$10^3 \sin^2 \vartheta/2$ reduced to $\text{CuK}\alpha$
Aequator									
$l = 0$	1.28	VW	66	62	110		1.63	W	66
	1.81	WM	129	124	200		2.35	W	133
	2.62	VS	256	248	220		3.41	VS	256
	—	—	—	495	400		5.45	S	504
	4.53	S	630	618	420				
1st zone									
$l = 1$	—	—	—	35	101		1.25	VVW	41
	2.06	M	167	159	211		2.64	S	166
	3.46	WM	416	406	321		4.67	MS	415
	4.08	W	540	530	411		5.81	MS+	536
	5.41	VW	789	776	431				
2nd zone									
$l = 2$	1.30	S	82	77	112		1.69	S	84
	2.08	S ⁻	178	170	212		2.70	S	178
	2.66	W	272	263	222		3.50	W	270
	3.02	WM	336	324	312		3.99	M	330
	3.51	MS	427	417	322		4.78	MS	423
	4.15	M	553	541	412				
	4.31	VW	584	571	332				
	5.53	M	800	787	432				
	5.73	WM	830	818	512				
3rd zone									
$l = 3$	2.11	WM	196	189	213				
	3.60	WM	447	436	323				
	4.26	W	571	560	413				
	5.74	W	818	806	433				
4th zone									
$l = 4$	1.34	MS	128	124	114				
	3.19	S	380	370	314				
	4.62	MS	629	617	334				
5th zone									
$l = 5$	0.77	W	131	127	105				
	2.24	WM	258	250	215				
	3.89	WM	502	497	325				
	4.67	WM	627	621	415				

4. *Determination of the positions of the atoms in the unit cell.*

In order to determine the positions of the atoms a knowledge of the diffraction intensities from the various planes is necessary.

TABLE III. ROTATION-DIAGRAM ABOUT [010]; $\lambda = 2.286 \text{ \AA}$

	Distance in cm.	Intens.	$10^3 \sin^2 \frac{\theta}{2}$ observed	$10^3 \sin^2 \frac{\theta}{2}$ calculated	<i>hkl</i>
Aequator					
$k = 0$	2.76	VS	281	279)	105)
				275)	200)
	2.94	S	314	306)	006)
				308)	202)
	3.31	W	386	375	106
	4.14	S ⁻	553	543	008
	4.31	M	587	577	206
	4.54	S ⁻	632	624	301
1st zone $k = 1$.	4.67	S	657	649	302
	4.89	S ⁻	699	689)	207)
				689)	303)
	5.64	VS	827	815	208
	1.68	W	170	169	112
	2.51	M	278	272	114
	3.04	S	360	348)	115)
				352)	211)
	3.18	S	381	373)	016)
				375)	212)
	3.44	M	424	418	213
	3.82	W	490	478)	214)
				488)	017)
	4.25	W ⁺	564	550)	117)
				554)	215)
	4.81	M	656	646	216
	5.26	MS	725	717	312
	5.54	M	764	754	217
	6.04	VS	826	818	314

TABLE IV. ROTATION-DIAGRAM ABOUT $[110]$; $\lambda = 2.286 \text{ \AA}$

	Distance in cm.	Intens.	$10^3 \sin^2 \vartheta/2$ observed	$10^3 \sin^2 \vartheta/2$ calculated	hkl
Aequator					
$h + k = 0$	1.92	VW	145	135	004
				137	$\bar{1}\bar{1}0$
	2.14	VW	176	170	$\bar{1}\bar{1}2$
	2.77	M	283	273	$\bar{1}\bar{1}4$
	2.92	MS	311	306	006
	4.15	VS	555	543	008
				549	$\bar{2}\bar{2}0$
	4.31	WM	587	581	$\bar{2}\bar{2}2$
	5.85	VS	858	852	$\bar{2}\bar{2}6$
1st zone					
$h + k = 1$	3.11	S	358	352	$\bar{2}\bar{1}1$
	3.19	S	371	369	106
	3.48	M	426	418	$\bar{2}\bar{1}3$
	3.81	M	487	478	$\bar{2}\bar{1}4$
	4.20	W	561	555	$\bar{2}\bar{1}5$
	4.73	M	657	647	$\bar{2}\bar{1}6$
	5.32	S	756	753	$\bar{2}\bar{1}7$

A. With a strongly absorbing crystal as HgI_2 , it is impossible to draw conclusions from intensity-relations on rotation diagrams, without taking account of the influence of absorption. ¹⁾

This is obvious from the missing 400 reflection on the Cu-film about $[001]$, which is very strong on the corresponding Fe-film. Now on the Cu-film the angle of deviation ϑ is smaller than 45° ($10^3 \sin^2 \vartheta/2 = 495$) while on the Fe-film it is greater ($10^3 \sin^2 \vartheta/2 = 781$).

In the case of diffraction with Fe-rays, incidence and reflection take place through the same crystal-face (in casu 110); in the case of diffraction with Cu-rays this is impossible (see fig. 1) and the diffracted X-rays must pass through an edge of the crystal. Hence the reflected beam will be nearly totally absorbed except in the very nearest neighbourhood of the crystal-edge. ²⁾

¹⁾ A. E. VAN ARKEL, *Physica* **3** p. 76.

²⁾ Note added during correction. In a recent paper W. L. BRAGG and G. B. BROWN *Proc. Royal Soc.* **110**, 35 (1926) have drawn attention to this same fact.

For the same reason we should expect the 200 reflection to be absent. It was present however, though very faint. We cannot give an explanation of this fact; ostensibly the prism-sides had not crumbled off.

In the beginning of this investigation we had concluded wrongly that 400 did not reflect, or only faintly. With Cr-rays 400 cannot reflect ($\sin \vartheta > 1$), on the Cu-powder film 400 coincides with other reflections;

TABLE V. ROTATION-DIAGRAM ABOUT $[111]$; $\lambda = 2.286 \text{ \AA}$

	Distance in cm.	Intens.	$10^3 \sin^2 \vartheta/2$ observed	$10^3 \sin^2 \vartheta/2$ calculated	hkl
Aequator					
$h + k + l = 0$	2.17	MS	181	170	$\bar{1} \bar{1} 2$
	3.17	M	359	351	$2 \bar{1} \bar{1}$
	3.51	WM	425	417	$\bar{2} \bar{1} 3$
	4.14	VS	553	546	$2 \bar{2} 0$
	4.89	W	699	703	$\bar{3} 0 3$
	5.03	M	725	715	$\bar{3} 1 2$
	5.63	VS	825	816	$\bar{3} \bar{1} 4$
	6.16	MS	900	895	$\bar{3} 2 1$
1st zone					
$h + k + l = 1$	3.30	M	384	376	$\bar{2} 1 2$
	4.68	W	659	649	$3 0 \bar{2}$
2nd zone					
$h + k + l = 2$	2.02	MS	177	170	$1 \bar{1} 2$
	2.71	MS	285	273 } 274 }	$\bar{1} \bar{1} 4$ } $2 0 0$ }
	3.17	M	362	352	$2 \bar{1} 1$
	3.50	W	427	417	$\bar{2} 1 3$
	4.22	W	565	556	$\bar{2} \bar{1} 5$
	4.34	W	586	581	$\bar{2} 2 2$
	5.12	W	727	716	$3 1 \bar{2}$
	5.72	VS	820	817	$\bar{3} 1 4$
	5.92	S	857	852	$\bar{2} \bar{2} 6$

hence these photograms could not give any direct information. We had used this absence of 400 for some laborious calculations, which did not lead to any structure. On a photogram taken casually with Fe-radiation we found that 400 did reflect and even strongly.

TABLE VI. ROTATION-DIAGRAM ABOUT $[201]$; $\lambda = 2.286 \text{ \AA}$

	Distance in cm.	Intens.	$10^3 \sin^2 \frac{\theta}{2}$ observed	$10^3 \sin^2 \frac{\theta}{2}$ calculated	hkl
Aequator					
$2h + l = 0$	2.17	VS	180	170	$\bar{1}12$
	3.32	VS	388	376	$\bar{1}22$
	5.04	S	726	716	$\bar{1}32$
1st zone					
$2h + l = 1$	3.15	M	359	348 } 350 }	$20\bar{3}$ } $12\bar{1}$ }
	3.50	M	424	418	$21\bar{3}$
	4.54	VW	631	623 } 623 }	031 } $22\bar{3}$ }
2nd zone					
$2h + l = 2$	1.52	W	111	100	012
	2.71	S	283	272	$\bar{1}14$
	3.30	M	389	382	$21\bar{2}$
	5.72	VS	824	818	$31\bar{4}$
	5.98	S	859	852	$\bar{2}26$

Rotation-diagrams about $[100]$ were made from KI, to demonstrate once more on a crystal of known structure that one cannot conclude a structure-factor to be small when the reflection fails on a rotation-diagram. Exposures were made at first on crystals bounded by its ordinary cube-faces, and then with its edges ground off. It was to be expected that in the last case the (110) plane would have to suffer less from absorption. The result is given in table VII.

TABLE VII. KI ROTATION-DIAGRAM ABOUT $[100]$; $\lambda = 2.286 \text{ \AA}$

Plane	Structure-factor	Observed intensities		
		Cube face is reflecting face		Edges ground off
200	K + I	VVS	Boundary face is reflecting face	WM
220	Item	—	„Through an edge“	VS
400	„	VS	Boundary face is reflecting face	WM
420	„	VS	Not „through an edge“	VS
440	„	S	Not „through an edge“	S

In interpreting intensities of rotation-diagrams, not only for absorption but for the other influences as well, the factors must be used in their special forms as adapted to this method. So for planes belonging to the zone of the rotation-axis, instead of the powder factor $\frac{1}{\sin^2 \vartheta/2 \cos \vartheta/2}$ ¹⁾, a factor

$\frac{1}{\cos \vartheta/2}$ must be used for an imbedded crystal. For other planes a factor appears²⁾ originating from the resolution of the rotation-velocity parallel to the normal on the reflecting plane. We hope to revert to these intensity questions, investigating whether disturbing influences³⁾ can be limited sufficiently to make rotation-diagrams useful for intensity calculations.

B. Therefore we have based our calculations mainly upon intensity-data from powder-photograms. The exposures were made with *Cu*-, *Fe*- and *Cr*-radiation. The intensities were independent of the degree of fineness of the powder. The size of our coarsest powder was ± 0.005 mm. Our finest powder, obtained by pouring a methylalcoholic solution into water, was not greater than 0.001 mm.

The exposures with *Cu*-radiation were made with a thin *Ni*-plate to filter away the $\text{CuK}\beta$ rays. As contrasted with the *Cu*- and *Fe*-films, the *Cr*-exposures showed a strong general blackening; they could be used only to determine more accurately the place of the strongest lines. On the *Cu*-films readings could only be carried out well up to $10^3 \sin^2 \vartheta/2 = \pm 500$; at greater angles of deviation the lines grew broad and diffuse.

In table VIII the results of the measurements of the powder films are given. The mentioned values of $10^3 \sin^2 \vartheta/2$ are averaged over many films and are corrected for the thickness of the rod following GERLACH-PAULI.⁴⁾

In the 4th column the planes are given which may cause the diffraction line; in the 5th column the corresponding calculated values of $10^3 \sin^2 \vartheta/2$.

On the *Fe*-film, line $n^0.11$ is split up into two distinct lines of nearly the same intensity, with values of $10^3 \sin^2 \vartheta/2$ (reduced to *Cu*) 248 and 252 respectively.

C. Determination of structure.

HgI_2 crystallizes tetragonal holohedrally. From table I it follows that the unit-cell is not body-centred. Hence the structure must be one belonging to the space-groups $D_{4h}^1 \mp D_{4h}^{16}$ ⁵⁾.

¹⁾ In the literature this powder-formula is found used for rotation-diagrams i.a. O. HASSEL, Z. f. Kristallographie 61, 92 (1924), pag. 98.

²⁾ H. OTT, Z. f. Physik., 22, 201 (1924), pg. 212.

³⁾ H. OTT. l. c. pg. 202.

⁴⁾ W. GERLACH and O. PAULI. Z. f. Physik. 7, 117 (1921).

⁵⁾ P. NIGGLI. Geom. Kristalogr. d. Diskont. pg. 129.

R. W. G. WYCKOFF. The analytical expression of the theory of space groups.

TABLE VIII. POWDERFILM HgI_2 [CuK α].

N ^o .	Intensity	$10^3 \sin^2 \vartheta/2$ corrected	Possible planes	$10^3 \sin^2 \vartheta/2$ calculated
1	MS	35	100; 003; 101	31; 34; 35
2	S	47	102	46
3	M+	67	004; 110; 103; 111	61; 62; 65; 66
4	M+	78	112	77
5	VS	125	114; 200; 105; 201	123; 124; 126; 128
6	W	141	006; 202	139; 139
7	W+	161	203; 115; 211	158; 159; 159
8	S	172	106; 212	169; 170
9	W+	191	007; 213	187; 189
10	W	221	214; 107; 205	216; 221; 221
11 11b	M	252	{ ²⁴⁸ 252	246; 248; 250; 251
12				
12	W+	264	206; 222	262; 263
13	VW	279	108; 300; 301; 223	276; 278; 282; 282
14	M	297	216; 302	293; 294
15	W	325	312	324
16	W	344	109; 217; 313; 225	341; 343; 343; 344
17	MS+	373	208; 314; 119; 305	370; 370; 372; 374
18	W	384	00 10; 226	383; 386
19	VW	407	320; 321; 315	402; 405; 406
20	W+	419	306; 322	416; 417
21	W+	447	11 10; 316	445; 447
22	VW	467	324; 219; 307	463; 465; 466

Two molecules of HgI_2 must be placed in the unit-cell. Supposing that like atoms are equivalent, the mercury atoms must be placed in two-fold positions and the iodine atoms in four-fold ones.

A first selection of possible cases was based on the intensities of the planes $hk0$. The c -coordinate of the atoms is immaterial for the formation of their structure-factor. The possible 13 combinations as regards the a and b coordinates, are the following.

two-fold positions:

four-fold positions:

1	0 $\frac{1}{2}$	$\frac{1}{2}$ 0	0 $\frac{1}{2}$	0 $\frac{1}{2}$	$\frac{1}{2}$ 0	$\frac{1}{2}$ 0
2	"	"	u u	\bar{u} \bar{u}	u \bar{u}	\bar{u} u
3	"	"	u 0	\bar{u} 0	0 u	0 \bar{u}
4	"	"	0 0	0 0	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$
5	"	"	$\frac{1}{4}$ $\frac{1}{4}$	$\frac{3}{4}$ $\frac{3}{4}$	$\frac{1}{4}$ $\frac{3}{4}$	$\frac{3}{4}$ $\frac{1}{4}$
6	"	"	u u	\bar{u} \bar{u}	$u + \frac{1}{2}$ $\frac{1}{2} - u$	$\frac{1}{2} - u$ $u + \frac{1}{2}$
7	"	"	u $u + \frac{1}{2}$	\bar{u} $\frac{1}{2} - u$	$\frac{1}{2} - u$ u	$u + \frac{1}{2}$ \bar{u} ,
8	0 0	0 0	0 $\frac{1}{2}$	0 $\frac{1}{2}$	$\frac{1}{2}$ 0	$\frac{1}{2}$ 0
9	"	"	u u	\bar{u} \bar{u}	u \bar{u}	\bar{u} u
10	"	"	u 0	\bar{u} 0	0 u	0 \bar{u}
11	"	"	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$	$\frac{1}{2}$ $\frac{1}{2}$
12	"	"	u $\frac{1}{2}$	\bar{u} $\frac{1}{2}$	$\frac{1}{2}$ u	$\frac{1}{2}$ \bar{u}
13	"	"	0 0	0 0	0 0	0 0

The parameter u has a range from $0^\circ \rightarrow 180^\circ$ in the structures 2, 3, 9, 10 and 12, and a range $0^\circ \rightarrow 90^\circ$ in Nos. 6 and 7. Now for u such a value has to be evaluated, that the course of the intensities of the prism-planes appears. The approximate formula $I = \frac{vS^2}{\sin^2 \frac{\varphi}{2}}$ is used; in this formula S = structure-factor, v = number of planes-factor. The scattering power of Hg and I has been taken as proportional to the number of electrons per ion, 78 and 54 respectively. For these heavy atoms and long waves the ratio of the scattering powers of Hg and I may be taken as approximately independent of φ (see 4d).

The estimated intensities of the prism-planes are given in table IX.

These intensities have been derived from powder films and rotation-diagrams. On the powder films lines representing 210 and 310 were missing (See table VIII). About lines 5, 7 and 9 (table IX) nothing can be concluded from the powder-films; in their place lines have been observed which may be due to other reflections. The failure of these lines has been deduced from their non-observed intensity on rotation-diagrams (table I), in which the reflection did not pass through an edge. These reflections have been printed in fat type in table X. Column 2 gives the values of $\frac{\varphi}{2}$ for these reflections (which have nowhere been observed); column 5 gives the angle φ between reflecting plane and bounding plane. When $\frac{\varphi}{2} > \varphi$, the reflection does not pass through an edge and consequently should have been observed. The intensities of lines 1, 2 and 4 are obtained principally from rotation-diagrams about [001] (table I); lines 1 and 4 are reflections from the bounding plane, so that their relative intensities may be obtained safely from rotation-diagrams. Line 2 observed as faint, passes through an edge; hence it must be strong.

TABLE IX.

1	110	VW
2	200	$\pm S$
3	210	—
4	220	$\pm S$
5	300	—
6	310	—
7	320	—
8	400	Present
9	330	—
10	420	Present

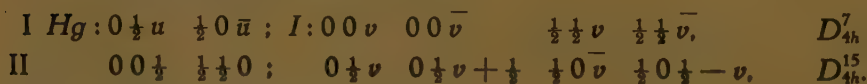
TABLE X.

Indices	$\frac{\varphi}{2}$			φ
	CuK	FeK	CrK	
210	23°	29°	36°	18°
300	32	41	51	45
310	34	45	56	26
320	39	53	71	11
330	48	70	—	0

With table IX the possible cases 1—13 have been examined with the following result:

1. This case is not possible as planes with h and k odd would have a structure-factor $= 2Hg + 4I$.
2. With the intensity ratio of 310 and 400 only $u < 30^\circ$ and $u > 150^\circ$ is consistent. This case is derived from D_{4h}^1 , in which 4 I-atoms have the same c -coordinate; hence their mutual distance should be smaller than 0.8 \AA . This must be considered as impossible, as, according to BRAGG¹⁾ the atomic radius of I is equal to 1.40° \AA .
3. To be rejected on the intensity ratio of 110, 200, 210, and 310.
4. Cannot be rejected.
5. This gives $S_{200} = 2Hg - 4I$, which is too small.
6. From the intensities 310 and 400 follows $u < 30^\circ$ and $u > 150^\circ$. This case is derived from D_{4h}^{14} , in which only 0 and $\frac{1}{2}$ figure in the c -coordinates. To be rejected because of the relative intensities of 102 and 104, 300 and 302, 210 and 212 etc.
7. To be rejected from the intensities of 110 and 200.
8. 300 is calculated too strong.
9. To be rejected from the intensities of 110 and 200.
10. To be rejected from the intensities of 110, 200 and 300.
11. Same as 1.
12. Impossible on account of the intensities of 110, 200 and 210.
13. Impossible because all structure-factors are equal to $2Hg + 4I$.

Finally only the fourth case remains, which is found to be derived from the following two structures:



¹⁾ W. L. BRAGG. Phil. Mag. 40, 169 (1920).

(In II the b -axis is shifted $1/2$ with respect to case 4)¹⁾.

I. Here the structure-factor reads:

$$S = Hg \{ (-1)^k e^{2\pi i l u} + (-1)^h e^{-2\pi i l u} \} + 2I \{ 1 + (-1)^{h+k} \} \cos 2\pi l v.$$

Now all possible structure-factors can be divided into three groups, viz.:

$$\text{for the planes } pil: S_{pil} = Hg \sin 2\pi u l$$

$$\text{" " " } ppl: S_{ppl} = Hg \cos 2\pi u l + 2I \cos 2\pi v l$$

$$\text{" " " } iil: S_{iil} = Hg \cos 2\pi u l - 2I \cos 2\pi v l.$$

Here i represents an odd index; p an even one.

If the reflections observed on the rotation-diagrams are arranged in these groups, a dependance of their intensities on l only should appear in each group (apart of course from the influence of absorption etc.).

Now this happens to be the case in all planes viz.:

$$pi\ 2 \text{ rather strong} \qquad pi\ 4 \text{ missing}$$

$$pp\ 2 \text{ missing or very faint} \quad pp\ 4 \text{ missing}$$

$$ii\ 2 \text{ rather strong} \qquad ii\ 4 \text{ very strong.}$$

It is not difficult to enclose u and v between rather narrow limits with the help of these data and the fact that 102 is a strong line on the powder film, while 104 fails.

Further calculations, which are omitted to save space, show however that no values of u and v can be found giving reasonable agreement with the observed powder-intensities.

II. This structure is identical with the somewhat simpler form:

$$Hg: 000 \ \frac{1}{2} \frac{1}{2} \frac{1}{2}; I: 0 \frac{1}{2} v \ 0 \frac{1}{2} v + \frac{1}{2} \ \frac{1}{2} 0 \bar{v} \ \frac{1}{2} 0 \frac{1}{2} - v.$$

Here too, just as in A , only the c -coordinate contains the parameter and the same splitting up of the structure-factor into three groups can be carried out:

$$S_{pil} = Hg \{ 1 - (-1)^l \} + 2iI \{ 1 + (-1)^l \} \sin 2\pi v l$$

$$S_{ppl} = Hg \{ 1 + (-1)^l \} + 2I \{ 1 + (-1)^l \} \cos 2\pi v l$$

$$S_{iil} = Hg \{ 1 + (-1)^l \} - 2I \{ 1 + (-1)^l \} \cos 2\pi v l.$$

According to these formulae the structure-factors of all planes ppi and iii are zero. Indeed, all these planes are absent on the rotation-diagrams.

Referring to the table above we find the following conditions:

$$S_{pi2} = 2I \sin 2v, \text{ moderate}$$

$$S_{pi4} = 2I \sin 4v, \text{ small}$$

$$S_{pp2} = Hg + 2I \cos 2v, \text{ small}$$

$$S_{pp4} = Hg + 2I \cos 4v, \text{ small}$$

$$S_{ii2} = Hg - 2I \cos v, \text{ moderate}$$

$$S_{ii4} = Hg - 2I \cos 4v, \text{ large.}$$

From the intensities of 102 and 104 on the powder-film, strong and not observed respectively, it follows that the intensity of 102 must be rather smaller than 104β . Hence we may require $I_{104} < \frac{1}{5} I_{102}$. From this

¹⁾ Notation see WIJCKOFF l. c.

inequality it follows that $\sin 2\nu > 1.5 \sin 4\nu$ and hence in the range of ν to be considered: $35^\circ < \nu < 55^\circ$. For different values of ν between these limits, the intensities of the powder film were calculated. The value $\nu = 50^\circ$ proved to agree very well with the observed intensities, as will be seen from table XI. The intensities, as given in the third column, are calculated from $I = \frac{\nu S^2}{\sin^2 \frac{\nu}{2}} \frac{1 + \cos^2 \frac{\nu}{2}}{\cos \frac{\nu}{2}}$.

In S we have taken $Hg = 2.9$ and $I = 2$, which agrees with the ratio of the number of electrons in Hg^{++} and I^- ions. ν is the number-of-plane-factor which equals 16 for planes hkl ; 2 for $00l$; 4 for $h00$ and $hh0$; and 8 for hkl , $h0l$ and hhl .

The first column of table XI gives all possible combinations of indices, only the planes of the form iii and ppi are omitted, their structure

TABLE XI. POWDERFILM RED HgI_2 $CuKa$.

Indices	Intens. observed	Intens. calculated	Indices	Intens. observed	Intens. calculated	Indices	Intens. observed	Intens. calculated
100	MS	0	214	W	0.2	208	MS+	1.1
101		3.7	107		0.5	314		2.6
102	S	4.8	008	W	0.4	305	W	0.2
004		0	220		1.1	00 10		0
110	M+	0.1	215	W	0.8	226	W	0.7
103		1.8	206		1.0	320	VW	0
112	M+	2.4	222	W+	0.2	321		0.5
104		0.27	108		0.3	10 10	—	0.1
114	VS	4.9	300	VW	0	306		0.3
200		2.6	301		0.3	322	W+	1.1
105	W	0.9	216	M	0.9	323		0.4
006		0.55	302		0.6	11 10	W+	0.9
202	—	0.45	118	—	0	316		0.1
210		0	224		0.03	324	VW	0.1
211	W+	1.3	310	—	0.03	219		0.4
106		0.9	303		0.3	307	—	0.2
212	S	2.3	312	W	0.9			
204		0.03	304		0.06			
213	W+	1.1	109	W	0.3			
116		0.06	217		0.5			

factor being identically equal to zero and none of these reflections having been observed.

D. Influence of the dependance of the scattering power on the angle of deviation.

In calculating the above intensities, the influence of heat-motion, the absorption in the rod and the dependance of scattering power on ϑ are neglected. Hence only intensity-ratio's of lines lying not too far apart may be compared. We tested whether, taking into account this dependance, anything is changed in the intensity-ratio's given in table XI.

An approximate idea of this dependance could be obtained from a paper by HARTREE¹⁾. In our case the ratio of the scattering powers appears to be sufficiently constant to neglect its change, comparing only lines not too far apart. This now is required because of the neglect of the absorption in the rod, which cannot be calculated accurately for a heavy powder.

5. Accuracy of the determination of the parameter.

The parameter ν can be determined with fairly great accuracy. Indeed $\nu = 53^\circ$ is eliminated since for the successive lines 13 v.w., 14 m. and 15 w., the intensities are calculated as 0,9, 1,1 and 1,5 respectively. On the other hand, with $\nu = 47^\circ$ line 18 is calculated weaker than line 19. Hence we may put $\nu = 50^\circ \pm 2,5^\circ$. We have ascertained that these limits do not alter with permissible changes in the ratio of the scattering powers.

6. Discussion of the structure.

Our structure is built up of layers of HgI_2 , in which each Hg-ion is surrounded nearly tetrahedrally by four I-ions. The distance between a Hg-ion and an adjacent I-ion (2,80 Å) agrees tolerably well with the sum of the atomic radii, respectively amounting to 1,50 Å for Hg in cubic HgS ²⁾ and 1,40 Å for I in the alkali-halides³⁾. The distance between successive layers is very large; the distance from an I atom in one layer to the neighbouring Hg-ion in the next layer amounting to 4,98 Å.

Apart from the fact that the Hg-ions are not surrounded exactly tetrahedrally by I-ions, the structure changes into the fluorspar-type by compressing the layers in the direction of the c-axis. This is shown on the plate, in which A represents the cell described above containing two molecules, B the crystallographic cell having the basal-diagonal of A for side and hence containing 4 molecules; C the fluorspar-structure obtained by compressing the layers.

¹⁾ D. R. HARTREE, Phil. Mag. **50**, 289 (1925).

²⁾ N. H. KÖLMEYER, J. M. BIJVOET en A. KARSEN. Rec. trav. Chim. **43**, 677 (1924).

³⁾ W. L. BRAGG, Phil. Mag. **40**, 169 (1920).

As regards the I-ions, the dimensions of this structure agree remarkably well with those found in SnI_4 ¹⁾ and in CdI_2 ²⁾. In these structures also



a.

b.

c.

the shortest distance in one layer between an I-ion and the adjacent positive ion is in agreement with BRAGG's values for the atomic radii; the distance between two I-ions in successive layers is equal to $4,18 \text{ \AA}$ in case of HgI_2 , while it amounts to $4,21 \text{ \AA}$ in both SnI_4 and CdI_2 .

According to HUND ³⁾ these layer-structures should be ascribed probably to the great extent to which the ions can be polarized; in our case it must be the I-ion, for which this has been found already in quite another way ⁴⁾. Under the influence of the adjacent Hg-ions the I-ion will behave as a doublet, pointing with its positive charge to the next layer. So with large polarisability the layer-structure should be the stable one, having less energy than the more compact, but unpolarised fluorspar-type. This is in analogy with the calculated case that amongst the rod-models of the water-molecule the compact symmetrical model should be stable with small polarisability, whereas an asymmetrical model should be stable in the opposite case ⁵⁾.

The formation of layers in this structure easily accounts for the perfect basal cleavage.

According to GROTH ⁶⁾ HgI_2 crystals crystallised from acetone,

¹⁾ R. G. DICKINSON. Journ. Am. Chem. Soc. **45**, 958 (1923).

²⁾ R. H. BOZORTH. Journ. Am. Chem. Soc. **44**, 2232 (1922).

³⁾ F. HUND. Phys. Z. **26**, 683 (1925).

⁴⁾ M. BORN et W. HEISENBERG. Z. f. Physik. **23**, 388 (1924).

⁵⁾ W. HEISENBERG. Z. f. Physik **26**, 196 (1924), F. HUND id. **31**, 81 (1925).

⁶⁾ P. GROTH. Chemische kristallographie I, pg. 218.

showed bi-axial birefringence and lamellar-structure with mutually perpendicular basal-directions. In connection with MALLARD's hypothesis that higher-symmetric crystals should be considered as polysynthetic twins of lower-symmetric lamels ¹⁾, it is obvious to suppose the elementary cell of HgI_2 to be rhombic and the crystal structure pseudotetragonal. During our X-ray investigation of crystals crystallised from methyl iodide no indication of this supposed pseudo-tetragonality was found. The cell dimensions at least can differ only very little from those given above. We intend to investigate these anomalous crystals.

7. Summary.

Red tetragonal holohedral HgI_2 has been investigated with X-rays by the rotating-crystal- and the powder method. Photograms were made with copper-, iron-, and chromium radiation. The cell dimensions are $a = 4,38 \text{ \AA}$, $c = 12,43 \text{ \AA}$, with 2 molecules to the unit-cell. The density is calculated as 6,28 in good agreement with the values given in the literature 6,28 to 6,30.

Amongst all possible holohedral space-groups only D_{4H}^{15} fits the observed intensities. The atomic positions are:

$$\text{Hg} : 000 \quad \frac{1}{2} \frac{1}{2} \frac{1}{2}$$

$$\text{I} : 0 \frac{1}{2} v \quad 0 \frac{1}{2} v + \frac{1}{2} \quad \frac{1}{2} 0 \bar{v} \quad \frac{1}{2} 0 \frac{1}{2} - v \quad \text{with } v = \frac{50 \pm 2,5}{360}.$$

The influence of the dependance of the scattering power on the angle of deviation has been considered. Table XI gives the observed and calculated intensities; the agreement is very good.

On the plate *A* gives the above structure, *B* the crystallographic cell containing 4 molecules. The Hg-ions are arranged in a body-centred lattice; each Hg-ion is surrounded nearly tetrahedrally by four I-ions. The structure can be changed into the fluorspar-structure by compressing the layers in the direction of the *c*-axis. (Plate: $B \rightarrow C$). In the alkali-iodides the negative I-ion is surrounded evenly all-round by positive ions. In HgI_2 however among the four Hg-ions surrounding each I-ion, two are lying at a distance of $2,80 \text{ \AA}$, agreeing with the sum of the atomic radii, while the other two are at the much greater distance of $4,98 \text{ \AA}$. The shortest distance between two I-ions in successive layers ($= 4,18 \text{ \AA}$) agrees remarkably well with the same distance in SnI_4 and CdI_2 (in both $4,21 \text{ \AA}$).

By the arrangement in layers the excellent basal cleavage is readily explained. The stability of the open marshalling may be explained, according to HUND, by taking into account the polarisation of the I-ion.

In interpreting our photograms the structure was assumed to be holohedral. Complete agreement between observation and calculation being obtained, no indication was found of a supposed pseudo-tetragonality of the structure.

¹⁾ F. M. JAEGER. Inleiding tot de studie der kristalkunde, pg. 202.

The smallness of the structure-factor of a plane may be deduced from the absence of the reflection on rotation-diagrams, only when the reflection does not pass "through an edge".

A considerable amount of the experimental work in this investigation has been done with great ability by our amanuensis A. KREUGER.

We are indebted to Prof. SMITS for his kind interest.

*Lab. of General and Inorganic
Chemistry of the University.*

Amsterdam, January 25th 1926.

Note added June 2nd.

In the Physical Laboratory of the University Manchester one of us (A. C.) made some measurements on HgI_2 with the X -ray spectrometer, mainly to determine more accurately the dimensions of the unit cell. These were found to be: $a = 4.357 \text{ \AA}$; $c = 12.36 \text{ \AA}$, accurate to about 0.1% and fully agreeing with recent data of HAVIGHURST (*Am. J. Science* **10**, 556 (1925): $a = 4.356 \text{ \AA}$; $c = 12.34 \text{ \AA}$), which reached us in the mean-time.

The intensity of reflexion of $\text{MoK}\alpha$ -rays from (110) and (001) planes is given below. As only small crystals were available only qualitative measurements were made.

	$\sin \frac{\theta}{2}$	Intens.		$\sin \frac{\theta}{2}$	Intens.
110	0.11	vvw	002	0.06	m
220	0.23	vs	004	0.12	—
330	0.34	—	006	0.17	s—
440	0.46	vw	008	0.23	s
			0010	0.29	—
			0012	0.35	—
			0014	0.40	w

Especially the intensities of the (001) reflexions confirm fully the above structure.

The powder-intensities given by HAVIGHURST agree well with ours. He made no attempt to locate the atoms.

moment t , exactly would be balanced by the heat developed in the wire (hence in this equation θ' has to be considered as a given function of t , which can be calculated as soon as the velocity is known);

λ = a coefficient, which approximately is given by the expression:

$$\lambda = \frac{0,24 i^2 R_0}{C\theta} (2)$$

in which i is the intensity of the electric current through the wire (it is supposed that i is invariable, which can be obtained by inserting a resistance of sufficient magnitude in series with the wire); R_0 is the resistance of the wire at the temperature of the air, and C is the heat capacity of the wire.

It will be seen that λ is independent of the length of the wire, as both R_0 and C are proportional to the latter quantity.

The formula is deduced from the equation:

$$C \frac{d\theta}{dt} = 0,24 r^2 R(\theta) - Q(U, \theta) \quad (3)$$

in which $Q(U, \theta)$ designs the heat lost per second by the wire, when exposed to an air current of velocity U . As θ' is defined by the equation:

$$0,24 i^2 R(\theta') = Q(U, \theta').$$

we may write the right hand side of (3):

$$0,24 i^2 \frac{dR}{d\theta} (\theta - \theta') - \frac{\partial Q}{\partial \theta} (\theta - \theta') \dots \dots \dots (4)$$

Now according to the theory of the hot wire anemometer as developed by KING ¹⁾, Q is proportional to θ , and thus $\partial Q / \partial \theta = Q / \theta = 0,24 i^2 R / \theta$. This transforms formula (4) into:

$$0,24 i^2 \left(\frac{dR}{d\theta} - \frac{R}{\theta} \right) (\theta - \theta') = \frac{0,24 i^2 (R - \theta dR/d\theta)}{\theta} (\theta' - \theta),$$

and so proves (2).

The formula, when applied to some types of wires which have been used, gives values of λ of the order of magnitude: 50, for wires of a diameter of 0,05 mm; 250, for wires of a diameter of 0,015 mm; 2000—5000, for wires of a diameter of 0,002 mm (supposing θ is about 500° C. in the former cases, but less in the latter case).

When it is supposed that the fluctuations of the velocity are produced by vortices, the axes of which are perpendicular to the direction of the mean motion, then the diameter of these vortices may be taken equal to 1 cm (or less) for a velocity of the air current of 10 m/sec — which is very well possible in the case of the motion in the boundary layer along a wall — and thus frequencies of the order of 1000 may

1). L. V. KING, On the convection of heat from small cylinders in a stream of fluid, etc., Phil. Trans. London, A 214, p. 373, 1914.

be expected. Only by using very thin wires, connected to very fast galvanometers (oscillographs), it will be possible to record such fluctuations.

The preliminary researches described in the following lines, however, have been executed with wires of 0,05 and 0,015 mm diameter; torsion string galvanometers, constructed by the N.V. v/h P. J. KIPP & ZONEN at Delft, have been used. These follow fluctuations with frequencies up to about 50 per second, which correspond with regions of disturbance, the "wave length" of which (for an air velocity of 8 to 12 m/sec) is about 20 cm or more.

The experiments have been made in the wind channel of the Laboratory for Aerodynamics and Hydrodynamics of the Technical Highschool at Delft; the dimensions of this channel are as follows: section: 80 cm (square); length of the part destined for experiments: 400 cm; before entering this part the air strikes along a honeycomb or collector, consisting of two sets of copper blades, forming 100 square channels of 8 cm width and of a length of 25 cm.

In order to fix the position of any point in the channel, the following coordinate system will be used: the X axis from the honeycomb down stream along the channel; the Y axis horizontal from the wall on the side where the experimenter stands to the other wall; the Z axis vertical from the bottom to the top. The blades of the honeycomb consequently are lying in the planes: $Y=8, 16, \dots 72$ cm; resp. $Z=8, 16, \dots 72$ cm; they extend from $X=-25$ cm to $X=0$.

§ 2. Dimensions of the vortices in a direction perpendicular to that of the air current.

In order to get an idea of the lateral dimensions of the regions of disturbance two anemometers were used, with separate resistance measuring appliances. The motions of the mirrors of the two galvanometers were photographed simultaneously on the same strip of paper. The X and Z coordinates of the wires were equal; their distance $\Delta Y = Y_1 - Y_2$ could be altered, in order to find at what distance correlation between the fluctuations, as indicated by the two wires, still could be detected.

It appeared that this distance was of the order of magnitude of 1 or 2 cm. As an instance the curves obtained with $\Delta Y = 1$ cm ($X = 372$ cm; $Z = 40$ cm; no objects in the channel) have been reproduced in fig. 1. The mean velocity was 8,0 m/sec; the scale of the upper curve is: 1 mm = a change of velocity of 3,1 cm/sec; the scale of the lower curve: 1 mm = a change of velocity of 1,6 cm/sec (the scale has been determined according to the method described in § 5). Both wires had a diameter of 0,015 mm.

If the instantaneous value of the velocity is denoted by U , its mean value by \bar{U} , and if: $U = \bar{U} + u$, then the value of $\overline{u^2}$, as derived from the curves, is about 60 (cm/sec)². The correlation between the two curves is clearly visible. At smaller distances it increases considerably.

This result at the same time demonstrates that the wires used in these experiments may not have too great lengths; otherwise one end of the wire will reach into other regions of disturbance than the other. A length of 1 cm may be considered as an upper limit.

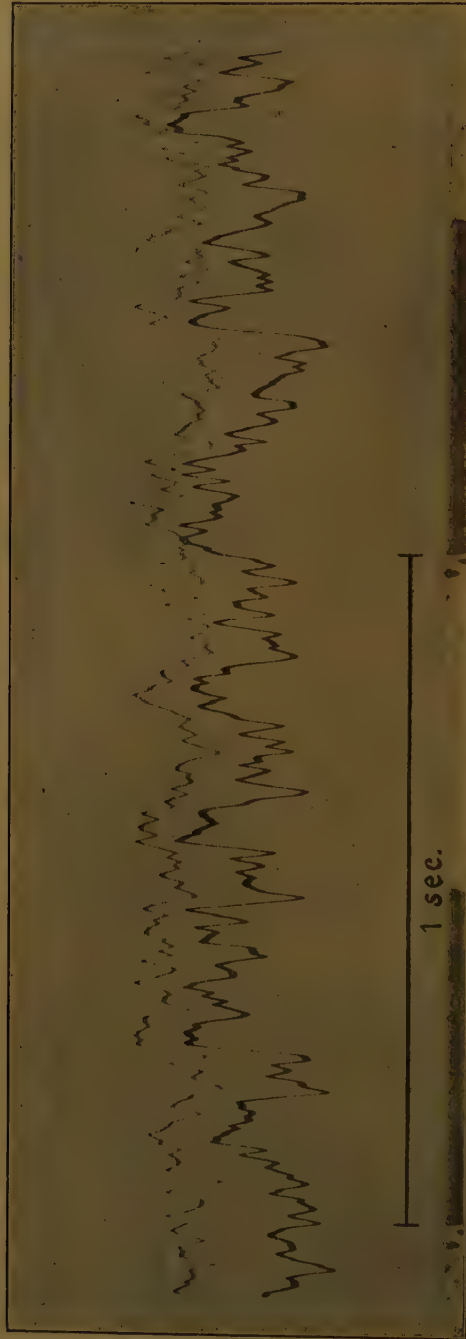


Fig. 1. Fluctuations of the velocity in two points lying 1 cm apart (measured in a direction normal to that of the mean motion of the air). Scale of the reproduction equal to that of the original record.

In the case of the motion in the boundary layer the dimensions in the direction perpendicular to the wall may be different from those in the direction parallel to the wall (but still perpendicular to the mean velocity). In order to study the distribution of the regions of disturbance along the length of the wire, a wire was used provided with six potential leads, spaced at distances of 5 mm (see fig. 2). By connecting compensational circuits with two pairs of potential leads, the simultaneous variations of the velocity at two points of the wire could be photographed. In one of the experiments executed the thickness of the

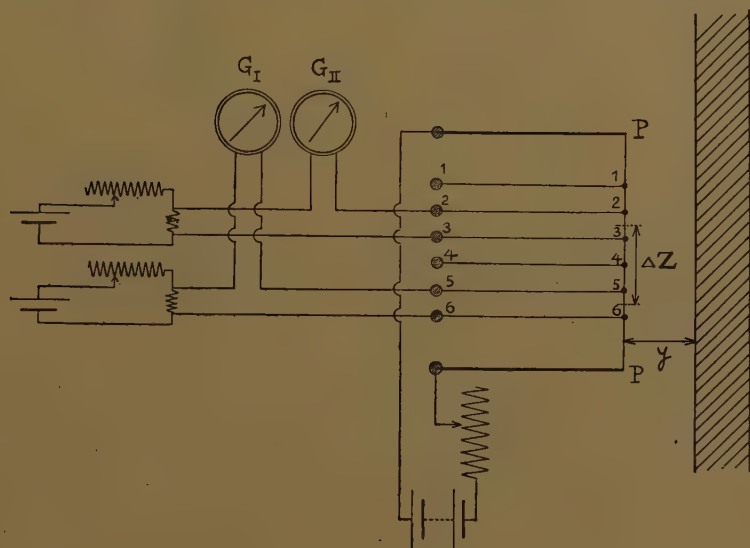


Fig. 2. Arrangement for the determination of the height of the regions of disturbance.

PP : electrically heated wire; 1-1, 2-2, ... 6-6: potential leads; compensational circuits have been connected to the pairs 2-3 and 5-6; G_I, G_{II} galvanometers; y : distance of the wire PP from the glassplate along which the boundary layer is formed; ΔZ : vertical distance of the points under observation.

boundary layer at the section where the wire was placed, was 2,2 cm; when the distance y of the wire from the wall amounted to 5,3 cm, the correlation could clearly be detected with $\Delta Z = 1,0$ cm, and was nearly absent with $\Delta Z = 2,0$ cm. However, when the distance y was less (1,0 cm), the correlation was clearly to be seen also with $\Delta Z = 2,0$ cm.

§ 3. Determination of the directional variations of the velocity.

When the distance between two wires is very small (0,2 or 0,1 mm), they will always be struck by the same regions of disturbance, and thus will show a perfect correlation. However, the two wires together now form an instrument which is sensitive to variations of the direction of

the air current. This is due to the circumstance that when the direction of the air current is not exactly normal to the plane of the two wires, hot air will be driven from the more exposed wire to the other, which is somewhat shielded by the former one, and in this way a difference of temperature is produced. In order to be able to determine simultaneously both the direction and the velocity of the current, the arrangement represented in fig. 3 may be used. It consists of two Wheatstone bridge circuits. The wires are denoted by P_1 and P_2 ; they are connected in series, so that the current through them is the same. w_1 and w_2 are

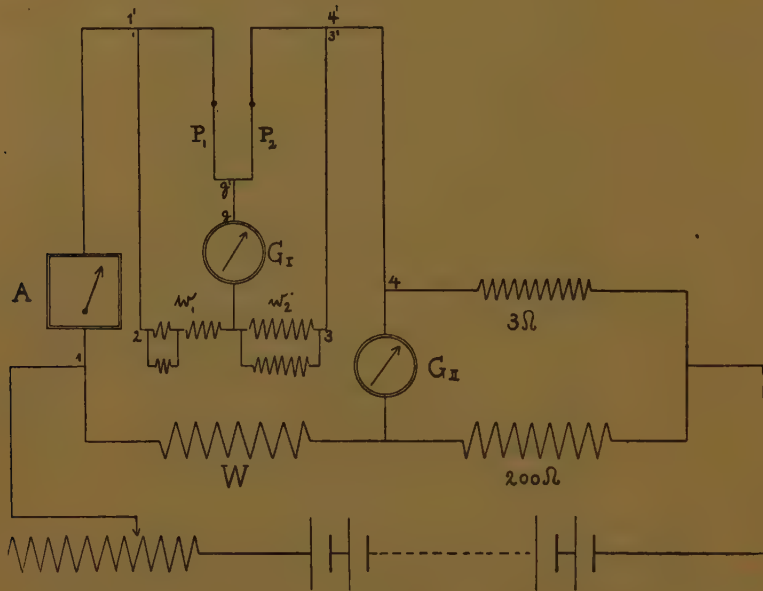


Fig. 3. Arrangement for the simultaneous observation of the variations of the direction and of the magnitude of the velocity.

approximately equal resistances, which can be altered by small amounts by means of shunts. The resistance W is determined in such a way that with a given value of the current through the wire and a given value of the air velocity, galvanometer G_{II} is in its zero point. The deviations of G_{II} from its zero point then show the fluctuations of the absolute value of the velocity. On the other hand galvanometer G_I shows the difference in temperature between the wires, and hence the directional deviations of the velocity. A is an ammeter.

The construction of the instrument is to be seen from fig. 4. A platinum wire in the form of a loop P_1P_2 is soldered to the points of two needles NN , which are fastened into the copper blocks BB , and are electrically isolated from each other. The loop is held tight by another loop, L , lying in a plane perpendicular to that of P_1P_2 , and made from a somewhat thicker wire, soldered to an elastic strip of german silver,

V ; it serves at the same time as galvanometer lead (g' in fig. 3). The ends of the wire P_1P_2 are soldered to those sides of the points of the needles which are turned to each other, and which have been filed down in some measure. In mounting the wire the distance of the two ends

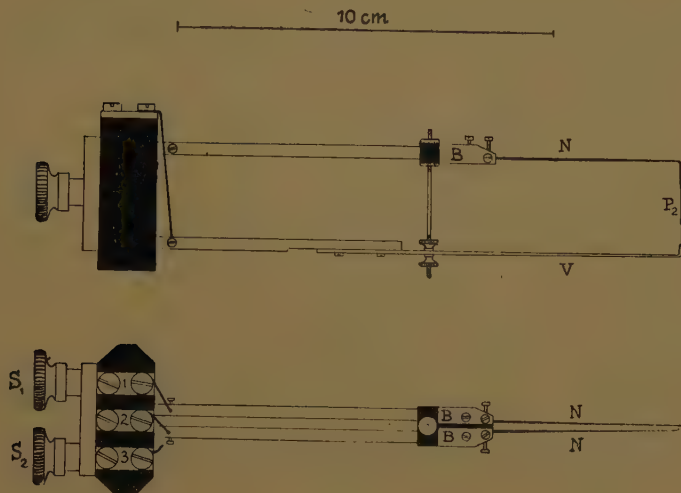


Fig. 4 a and b. Hot wire anemometer for the observations of variations both of direction and of magnitude of the velocity. The copper blocks 1, 2, 3 respectively are connected electrically with the ends P_1 and P_2 of the wire, and with the loop L .

forming the loop is regulated by hand by shifting the needles in the holes provided for them in the copper blocks BB ; then they are fastened by means of little screws, while with the aid of other screws the needles may be bent slightly, in order to bring their points exactly at the same height and in the same plane (the plane of fig. 4a). The instrument has been designed with a view of using it for measurements in the boundary layer along a glass plate, in which case the disturbance of the air current must be reduced to a minimum. The ends of the needles must not be connected; otherwise it would be impossible to stretch both wires at the same time.

By means of the screws S_1S_2 the anemometer was fastened to a vertical rod, which by means of a horizontal rod was connected to a second vertical rod. The latter rod could be rotated about its axis, and if the anemometer was mounted correctly the axis passed just between the two wires (which also were vertical). The angle of rotation could be read on a divided circle, fixed to this rod at the outside of the channel. In the normal position of the apparatus (0° or 180°) the plane of the wires (i. e. the plane of fig. 4a) was perpendicular to the axis of the wind channel. The whole arrangement could be moved in the Y direction

by means of a slide, provided with screw motion; the distance traversed was read on scales.

As the electrical measuring instruments were placed in an other room than that where the channel stands, the leads 1—1', 2—2', 3—3', 4—4' and $g-g'$ (cf. fig. 3) were rather long, and their resistance had to be taken into account when calculating the current through the wire. By way of example the principle data, referring to experiments executed Jan. 9th, 1926, are given here: distance of both ends of the wire: 0,12 mm; diameter of wire: 0,05 mm; length of each end: ca. 9 mm. Resistance of wire and leads 1'— P_1 — P_2 —4' during the experiments: 2,37 Ω ; at room temperature: 1,28 Ω ; w_1 and $w_2 =$ ca. 3 Ω ; $W = 172 \Omega$. Current through the wire for a mean velocity of the air equal to 11,4 m/sec: 0,90 Amp.; through the ammeter: 1,200 Amp.

§ 4. Calibration of the Anemometer.

A. Calibration for variations of direction.

At a given value U of the velocity of the air current, and a value i of the intensity of the electric current through the ammeter, the resistance W is regulated so that G_{II} is in its zero position; then the plane of the wires is set under various angles ($\alpha + 90^\circ$) to the direction of the air current, and for every position the value of $w_1 - w_2$ that brings G_I back to its zero point is determined. Observation of G_{II} at the same time will show whether the velocity determination is influenced or not by variations of the direction. A difficulty in these determinations is caused by the circumstance that the galvanometers never are wholly at rest, so that it is necessary to estimate their mean reading. The sensitivity therefore cannot be brought up to the highest possible value. The data mentioned below, which relate to experiments made Jan. 9th, 1926, do not pretend to be of high accuracy; their only aim is to give an idea of the sensitivity which can be obtained.

For angles between -10° and $+10^\circ$ the difference $w_1 - w_2$ which brings G_I back to its zero position is approximately a linear function of α . The sensitivity is somewhat greater for values of α between -5° and $+5^\circ$ than outside of this interval; the difference, however, is small. As a mean the formula was obtained:

$$w_1 - w_2 = 0,0040 \alpha + c \quad . \quad . \quad . \quad . \quad . \quad (5)$$

(w in Ω , α in degrees) with $U = 11,4$ m/sec, $i = 1,200$ Amp.; $W = 172 \Omega$. During the experiments c changed sometimes in an irregular manner with an amount of 0,004 Ω . There could not be detected any influence of α on the indication of G_{II} .

B. Calibration for variations of velocity.

These calibrations were executed with $\alpha = 0^\circ$; i is kept constant, and for various values of U the value of W is determined which brings

G_{II} into its zero point. It is necessary carefully to take notice of the value of i , as small variations of the intensity of the electric current may have an appreciable influence on the results. In order to reduce the disturbances due to such an effect, it may be preferred to give various fixed values to W , and to determine for each of these values the intensity i which brings G_{II} back to its zero point, as a function of U . By means of interpolation it is possible afterwards to obtain $(\partial W / \partial U)_{i=\text{const.}, G_{II}=0}$. W does not change linearly with U over great ranges. With $U = 11,4$ m/sec, $i = 1,200$ Amp. the mean value:

$$\partial W / \partial U = 0,015 \Omega \text{ per cm/sec}$$

was obtained.

During these measurements attention was paid to the galvanometer G_I and it was considered whether the value of $w_1 - w_2$ which for $\alpha = 0^\circ$ brings G_I into its zero position, systematically varied with the value of U or not. Such a variation might be produced by two causes. In the first place it may be expected that when the two ends of the wire are not mounted symmetrically, changes of temperature of the whole system will produce differences of temperature between the two ends. This can easily be detected when, for a constant value of U , the value of i is changed; in that case G_I might show a systematic variation dependent on i . When the plane of the two wires is not perpendicular to the direction of the air current, such an effect is clearly visible; it changes sign with the sign of the angle of deviation and the position can be found in which it disappears. If this position does not correspond to $\alpha = 0^\circ$, the plane of the wires has not the correct position in the apparatus, and must be altered by bending the needles slightly by means of the small screws provided for that purpose in the blocks BB .

In the second place the position of the needles relatively to each other might be changed by the pressure exerted on them by the air current. When the first mentioned effect had been eliminated, in some cases an influence of the value of U (at constant temperature of the wires) could be detected; it had the expected direction, but was very small (changes of c amounting to $0,002 \Omega$, corresponding to an angle of $1/2^\circ$, for changes of U from 10 to 13 m/sec)¹⁾.

§ 5. Scale of the galvanometers.

It has been mentioned that the motions of the mirrors of both galvanometers G_I , G_{II} were photographed simultaneously. The scales of the

¹⁾ With an anemometer having wires of 0,015 mm diameter, spaced 0,07 mm from each other, much greater disturbances due to this cause were observed. Therefore the needles, after having been brought to their correct position, have been connected firmly with each other by means of a drop of sealing wax. Besides before each new series of experiments it was necessary to inquire at what angle α the difference $w_1 - w_2$ appeared to be independent of U and of i . This angle then was chosen as the zero point of the directional calibration. (Note added in the proof).

curves thus obtained were derived from measurements of the deviations corresponding to known variations of $w_1 - w_2$ and of W . In order to get rid of the disturbances due to the fluctuations of the velocity of the air current, which cause a never ending oscillation of the mirrors, the wire was taken out of the connection during these determinations, and was replaced by two unvariable resistances of the correct magnitude. From the values of $(\partial G_I / \partial (w_1 - w_2))_{\alpha = \text{const.}}$, $(\partial G_{II} / \partial W)_{U = \text{const.}}$, found in this way, and from the values of $(\partial (w_1 - w_2) / \partial \alpha)_{G_I = 0}$, $(\partial W / \partial U)_{G_{II} = 0}$, deduced from the calibration of the anemometer, the scale of the curves is found by means of the formulae:

$$\frac{\partial G_I}{\partial \alpha} = - \frac{\partial G_I}{\partial (w_1 - w_2)} \frac{\partial (w_1 - w_2)}{\partial \alpha}; \quad \frac{dG_{II}}{dU} = - \frac{\partial G_{II}}{\partial W} \frac{\partial W}{\partial U}.$$

As U was equal to 11,4 m/sec, an angle α of $+1^\circ$ corresponded to a lateral component of the velocity $v = -20$ cm/sec (according to the direction of the Y axis, defined in § 1). The following values were obtained:

$$\partial G_I / \partial (w_1 - w_2) = 3600 \text{ mm}/\Omega; \quad \partial G_{II} / \partial W = 38 \text{ mm}/\Omega;$$

and hence:

$$\partial v / \partial G_I = 1,4 \text{ cm/sec per mm}; \quad \partial u / \partial G_{II} = 1,75 \text{ cm/sec per mm}.$$

§ 6. As an example of the application of the instrument some records have been reproduced (fig. 5) relating to the motion of the air behind the honeycomb. The coordinates of the pair of wires were: $X = 50$ cm; $Z = 44$ cm; Y resp. 36,0, 39,0, 40,0, 41,0 and 44,0 cm. The plane $Y = 40,0$ cm contains a blade of the honeycomb, hence in this plane \bar{U} will have a minimum value, whereas in the planes $Y = 36,0$ and $44,0$ cm \bar{U} will have maxima. The distribution of the velocity had already been determined on a former occasion by Dr. Ir. VAN DER HEGGE ZIJNEN, with the aid of a Pitot tube (for a mean velocity \bar{U} of 24 m/sec); it was found that the minima were rather narrow, the maxima very broad. The difference between the maximum and the minimum value of the velocity amounts to ca. 7 %.

The following peculiarities may be remarked in the records:

In the points of maximum velocity the amplitude of the u component (variation in the absolute value of the velocity) is small, that of the v component (directional variation) is great. The contrary takes place in the point of minimum velocity¹⁾. The records relating to the sloping

¹⁾ In order to keep the u -curve for $Y = 40,0$ cm within the field of the camera, the resistance W in this case was increased to 173Ω ; this caused a displacement of the curve (in the positive or upward direction) over 38 mm.

In the records for $Y = 36,0$ cm and for $Y = 44,0$ cm the mean ordinate of the u -curve is about 54 mm above the time mark; in the record for $Y = 40,0$ cm it is about 45 mm above it. Noticing the purposely applied displacement of 38 mm upwards in the latter case, it is found that in reality the u -curve has moved downwards over $54 - (45 - 38)$

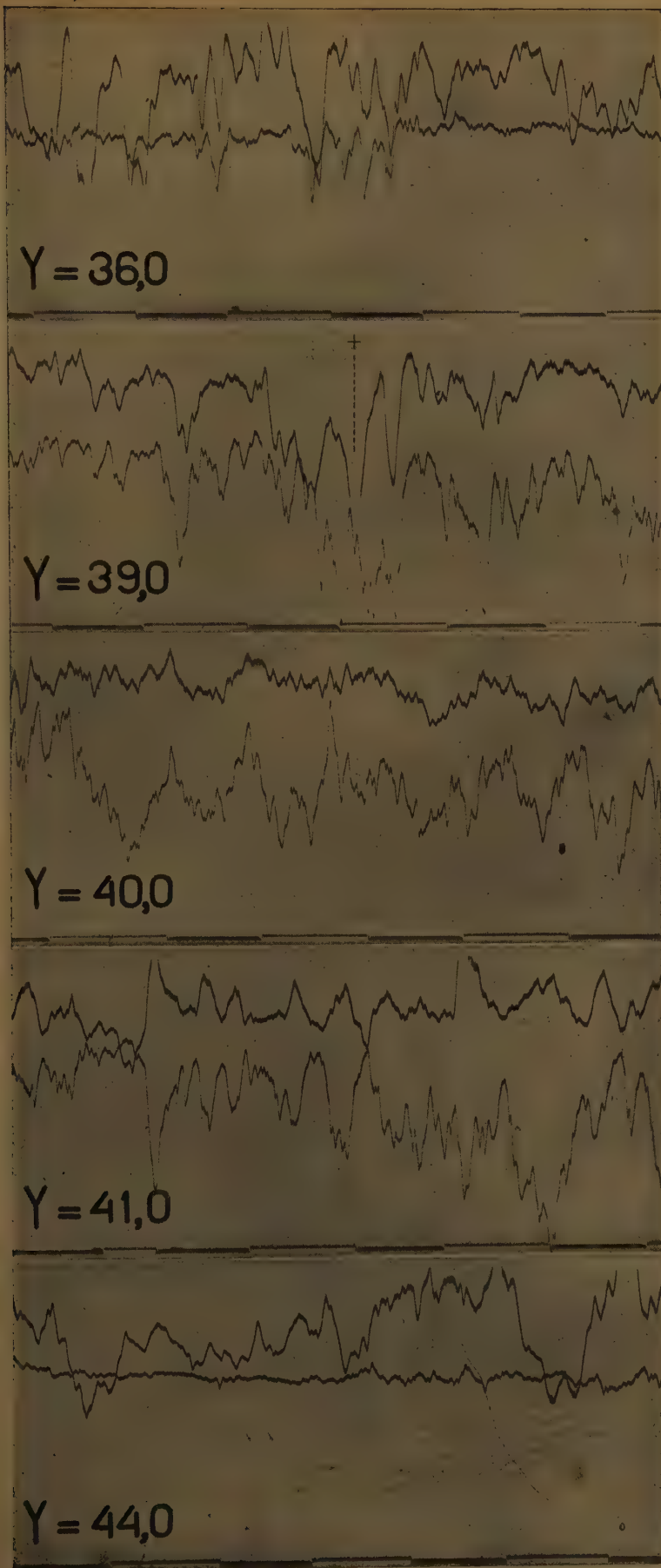


Fig. 5. Records of the variations of the u and v components of the velocity in points of the line $X = 50$ cm, $Z = 44$ cm in the wind channel. In every record the upper curve represents u , the lower one v ; the positive direction is always upwards. The curves have been reduced to $1/2$ their original size. The time mark — denotes 1 second (in the record for $Y = 41,0$ cm the first time mark has come too late).

parts of the velocity curve $\bar{U}(Y)$ clearly show a correlation between the variations of u and of v ; as could be expected this correlation is positive in the point $Y=39,0$ cm, and negative in the point $Y=41,0$ cm. The correlation is produced by the circumstance that those elements of fluid which pass through the point of observation in a direction, deviating from the normal or mean direction of the motion, have started from a layer of fluid, where the mean velocity was either greater or less than in the point of observation. Such a correlation is not present in the records relating to the maxima or minima of the velocity.¹⁾

It is possible to combine the fluctuations of u and those of v optically, by means of the same method which is used in demonstrating LISSAJOUS's curves. In this case the galvanometers are mounted in such a way that the plane of the motion of the mirror of one of them is perpendicular to the corresponding plane of the other; with the aid of a lense an image of the mirror of the first galvanometer is formed on the mirror of the second one, and the system is illuminated by one lamp. Then a spot of light can be projected on a screen, the horizontal motions of which for instance may correspond to the fluctuations of the u component, whilst the vertical motions correspond to the fluctuations of the v component. This affords an easy method of demonstrating the presence or absence of correlation between the two components.²⁾

= 47 mm. This corresponds with a decrease of velocity of about 80 cm/sec; hence the 7 0/0 difference in velocity between the maxima and minima which has been mentioned in the text.

In the records for $Y=39,0$ cm and for 41,0 cm the mean ordinate of the u -curve is only little below that of the u -curve in the records relating to the maxima of the velocity.

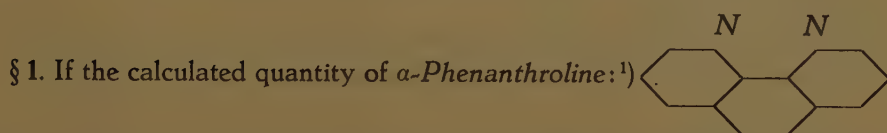
1) Sometimes a correlation between the u and the v components was observed in the point $Y=40,0$ cm. This may be ascribed to the fact that the direction of the mean current in the channel sometimes deviated from that of the X -axis, owing to disturbances originating in the room where the channel was placed (indications of such an effect have been observed also during other experiments). In such a case the minimum of velocity would not lie in the point $Y=40,0$ cm but somewhat to the right or to the left of it.

The point marked + in the record for $Y=39,0$ cm is of some interest: here a considerable negative value of v (angle of deviation about 3° or 4°) is accompanied by an increase of the u component; it may be supposed that in this instant the air moving through the point of observation had started from a layer already beyond the layer of the minimum velocity, for instance from the layer $Y=40,5$ cm. It has to be observed that the mean free path of a mass of air (measured in the direction of Y) under the circumstances of the experiment is comparable to the distance between the layers of maximum and of minimum velocity.

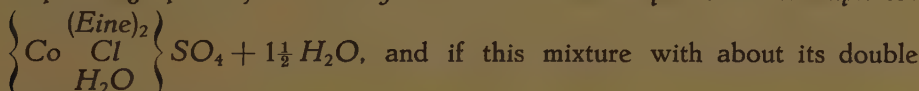
2) An instance of correlation between variations in direction and in magnitude at an atmospheric scale may be found in an anemometer diagram of Marshside, Southport, of Jan. 6—7, 1907, reproduced in the Technical Report of the Advis. Committee for Aeronautics, London, 1909—10, p. 98 and figs. 15^a and 15^b.

Chemistry. — “On racemic and optically-active α -Phenanthroline-diethylenediamine-Cobaltic-Salts and on the Reaction between Mono- or Diamines and Diethylenediamine-dichloro- or -chloro-aquo-Salts.” By Prof. F. M. JAEGER.

(Communicated at the meeting of February 27, 1926).



mpt.: 173° C., prepared after BLAU's method²⁾, be added to the corresponding quantity of Diethylenediamine-chloro-aquo-Cobaltic-sulphate:



weight of water be heated during 6 or 8 hours with a small flame in a flask with hemi-spherical bottom and provided with a reflux-cooler, — the original lilac-red colour of the solution gradually changes into a yellowish-brown one. After cooling during 24 hours, small brownish-yellow, thin, tabular crystals are deposited, while by careful evaporation of the mother-liquor again a fresh quantity of the same salt may be obtained. Finally a viscous liquid remains, from which a small quantity of small, dark-brown crystals are deposited, but which does not completely crystallize, even after a long time. The first deposited, brownish-yellow product appears to be a Chlorosulphate of an α -Phenanthroline-diethylenediamine-Cobaltic ion. The salt can be purified by recrystallisation; it is finally obtained in the shape of beautiful, very brittle, gold-yellow needles, united in clusters, and showing the composition:



evaporation of its solutions can be obtained in thicker needles, it is, however, not possible to study them accurately, because they have strongly varying angular values and, moreover, do not possess sufficiently developed terminal facets. The needles are triclinic, have oblique and mostly un-

¹⁾ The base is also called: Pseudo-phenanthroline and crystallizes with 4 H₂O, which it loses, however, by heating at 100° C.

²⁾ F. BLAU; Monatshefte, 19, 647, (1898).

dulatory extinction and are only feebly dichroitic. In one of the terminal zones angles of $83^{\circ}25'$, $33^{\circ}16'$ and $63^{\circ}12'$ were measured; in the vertical zone such of 86° or 87° , and of 16° , 24° and 63° . The complex ion is precipitated by a solution of NaI in the form of an orange coloured iodide, which is sparingly soluble in water, and which by slow evaporation of its only very weakly concentrated solution, can be obtained in the form of small, dark brown crystals. They are anhydrous and have the composition: $\left\{ \text{Co} \begin{smallmatrix} (\alpha\text{-Phen}) \\ (\text{Eine})_2 \end{smallmatrix} \right\} I_3$; their full description is given further on.

The dark brown crystals, however, which were obtained from the mother-liquor, were proved to be for the greater part such of *Triethylenediamine-Cobaltic-chlorosulphate*, with its characteristic *ditrighonal-scalenohedral* crystalform: finally the viscous mother-liquor gives by precipitation with NaI , moreover, an iodide, which could be obtained, on slow evaporation, in measurable crystals, which appeared to be identical with those of *racemic Triethylenediamine-Cobaltic-iodide*.

From this it is evident, that the complex *Diethylenediamine-chloro-aquo-Cobaltic-ion* is partially decomposed during the reaction, with simultaneous formation of the apparently highly stable *Triethylenediamine-ion*; partially, however, the reaction has occurred in the normal way, i.e. by substitution of the H_2O -group and the Cl -atom of the complex-ion by one molecule of α -Phenanthroline.

Analysis of α -Phenanthroline-diethylenediamine-Cobaltic-chlorosulphate: 0,2820 gramme of the substance gave 0,1246 gramme $BaSO_4$ and 0,0794 gramme $AgCl$. Therefore: 6,96% Cl and 18,2% (SO_4) . The determination of the water-content gave: 6,81% H_2O .

Calculated for $\left\{ \text{Co} \begin{smallmatrix} (\alpha\text{-Phen}) \\ (\text{Eine})_2 \end{smallmatrix} \right\} Cl (SO_4) + 2 H_2O$: 6,83% H_2O ; 6,74% Cl and 18,23% (SO_4) .

The Iodide gave in the same way: 51,3% I ; calculated for $\left\{ \text{Co} \begin{smallmatrix} (\alpha\text{-Phen}) \\ (\text{Eine})_2 \end{smallmatrix} \right\} I_3$: 51,49% I .

The compound was anhydrous and only very sparingly soluble in water.

The last mother-liquor but one gave dark brown crystals of *rhombic-bipyramidal* symmetry; forms observed: $c = \{001\}$, predominant; $s = \{021\}$ and $q = \{041\}$, the last form much broader than s ; $o = \{111\}$, well developed; $\omega = \{221\}$, narrow; $\delta = \{113\}$, extremely narrow. The following measurements were made: $c : o = 53^{\circ}10'$; $c : q = 73^{\circ}39'$; $c : s = 60^{\circ}$; $o : o' = 74^{\circ}50'$; $o : o_4 = 62^{\circ}27'$; $o : q = 48^{\circ}18'$. The habitus of the crystals is elongated parallel to the a -axis, with flattening parallel $\{001\}$. Later also small octahedral-shaped crystals were obtained, which showed only $o = \{111\}$ and, very small, $c = \{001\}$. From the last mother-liquor thick, kite-shaped crystals were obtained, which showed $c = \{001\}$ very well developed, and furthermore: $o = \{111\}$, large and lustrous and $\omega = \{221\}$, very narrow. Measurements: $c : o = 53^{\circ}8'$; $o : o' = 74^{\circ}48'$; $o : \omega = 16^{\circ}3'$; $o : q = 48^{\circ}15'$. From these data it becomes evident that no other substance than racemic $\left\{ \text{Co} (\text{Eine})_3 \right\} I_3 + 1 H_2O$ is present here,

as described formerly¹⁾; in the measurements given formerly, the *c*-axis was taken with double the value adopted here.

Analysis: 59,9 0/0 I; calculated: 59,7 0/0.

§ 2. Crystalform of racemic $\left\{ \begin{matrix} \text{Co}^{(a-Phen)} \\ (\text{Eine})_2 \end{matrix} \right\} I_3$.

From water the salt is deposited in very small, brown crystals, which can accurately be measured (Fig. 1).

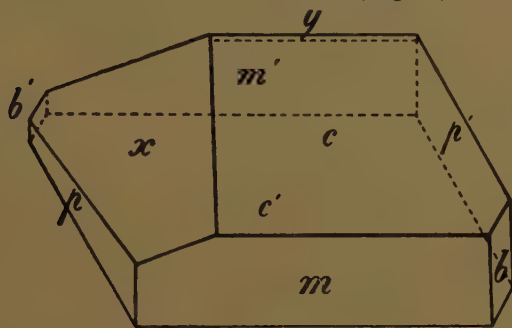


Fig. 1.

Triclinic-pedral.

$a : b : c = 0,6487 : 1 : 0,4692$;
 $A = 100^\circ 2\frac{1}{2}'$; $\alpha = 111^\circ 13\frac{1}{2}'$.
 $B = 121\ 9$; $\beta = 125\ 53$.
 $C = 75\ 53$; $\gamma = 66\ 39$.

Forms observed: $c = \{001\}$, lustrous, well developed, but smaller than $c' = \{001\}$, which form appears striated parallel to the edge $c' : p'$; $m = \{110\}$ and $p = \{110\}$, well developed

and lustrous; $m' = \{\bar{1}\bar{1}0\}$, is duller than m , and the same holds, in somewhat smaller degree, for $p' = \{\bar{1}\bar{1}0\}$; $b = \{010\}$ and $b' = \{0\bar{1}0\}$, very lustrous, but much narrower than m and p ; $y = \{\bar{1}\bar{1}1\}$, narrow but yielding good reflections; $x = \{149\}$, large and lustrous, but making rather varying angles with p , m and also with c . The habitus is tabular parallel to c' , with a slight elongation parallel to the edge $c : m$. No distinct cleavage was observed.

Angular values:

Observed: Calculated:

$m : p = (110) : (\bar{1}\bar{1}0) =$	58°	$3'$	—
$p : b' = (110) : (0\bar{1}0) =$	50	$12\frac{1}{2}$	—
$m : c = (110) : (001) =$	52	56	—
$p : c = (\bar{1}\bar{1}0) : (001) =$	70	37	—
$c : y = (001) : (\bar{1}\bar{1}1) =$	47	31	—
$b : m = (010) : (110) =$	71	$44\frac{1}{2}$	$71^\circ 44\frac{1}{2}'$
$c : x = (001) : (149) = \text{ca.}$	12	30	$12\ 20$
$m : x = (110) : (\bar{1}\bar{1}49) =$	53	55	$53\ 34$
$m' : y = (\bar{1}\bar{1}0) : (\bar{1}\bar{1}1) =$	79	33	$79\ 33$

On all faces oblique extinction. Strongly dichroitic: on x for vibrations almost parallel to the *a*-axis: orange, for such perpendicular to it: blood-red.

From these measurements it is clear that this iodide shows no form-analogy with that of the Triethylenediamine-Cobaltic-ion.

For a fuller description of the properties of the new complex-ion, also

¹⁾ F. M. JAEGER. Rec. des Trav. Chim. d. Pays-Bas, 38, 205, 206. (1919).

a number of some other salts were prepared by reaction of the *iodide* with different *silver-salts*. Besides the *chlorosulphate* and *iodide* already mentioned above, also the following salts were obtained in a well crystallized form: the *sulphate*, the *nitrate* and the *chlorate*, which salts crystallize respectively with 12, 0, and 1 molecules of water. Their crystalform is described below. Also the corresponding *bromide* was prepared by double decomposition with *AgBr* and evaporation of the solution. The crystallized salt is anhydrous, or contains perhaps 0,5 molecule H_2O . On slow evaporation of the solution only very thin needles are obtained, which are only rudimentarily developed and unsuitable for measurement.

§ 3. Crystalform of racemic $\left\{ \begin{matrix} \text{Co}^{(\alpha\text{-Phen})} \\ \text{(Eine)}_2 \end{matrix} \right\} (\text{NO}_3)_3$.

Beautiful, small, highly lustrous crystals were obtained from an aqueous solution, containing some *silvernitrate* in excess. (Fig. 2).

Triclinic-pedial.

$$a : b : c = 0,9938 : 1 : 0,8574;$$

$$A = 91^\circ 0' ; a = 88^\circ 22'.$$

$$B = 104\ 13 ; \beta = 104\ 16\frac{2}{3}.$$

$$C = 100\ 33 ; \gamma = 100\ 40.$$

Forms observed:

$a = \{100\}$, predominant, yielding very sharp images, sometimes striated diagonally; $a' = \{\bar{1}00\}$, also large and lustrous; $b' = \{010\}$, well developed and highly lustrous; $b' = \{0\bar{1}0\}$, narrow; $c = \{001\}$,

broader than b ; $c' = \{00\bar{1}\}$, narrower than c , but well reflecting; $r = \{\bar{1}01\}$, very sharply reflecting, narrower than c and than $s = \{10\bar{1}\}$, which form yields extremely good reflections; $m = \{110\}$, large, occasionally vertically striated; $p' = \{\bar{1}10\}$, narrow, but well measurable; $n' = \{\bar{1}\bar{1}0\}$, narrower than m , not striated and very lustrous; $q' = \{01\bar{1}\}$, eminently reflecting; $q = \{0\bar{1}\bar{1}\}$, smaller than q' , yielding good images; $t = \{302\}$, very narrow, but well measurable. The habitus of the crystals is thick tabular parallel $\{100\}$, sometimes prismatic parallel to the c -axis, but occasionally elongated in the direction of the b -axis.

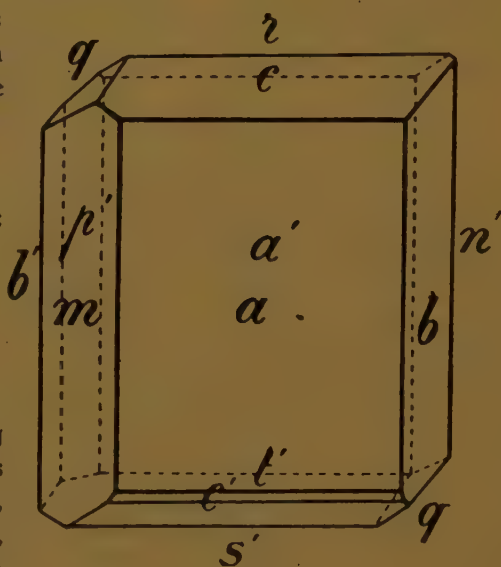


Fig. 2.

Angular values:

Observed: Calculated:

$a : b = (100) : (010) =$	$79^\circ\ 27'$	—
$a : c = (100) : (001) =$	$75\ 47$	—
$b : c = (010) : (001) =$	$89\ 0$	—

Angular values :

Observed : Calculated :

$a : m = (100) : (\bar{1}\bar{1}0) =$	*48	27	—
$c : r = (001) : (\bar{1}01) =$	*47	19	—
$b : n' = (010) : (\bar{1}\bar{1}0) =$	51	46	51° 21½'
$a' : p' = (\bar{1}00) : (\bar{1}\bar{1}0) =$	38	38	38 49
$p' : b' = (\bar{1}\bar{1}0) : (0\bar{1}0) =$	40	49	40 38
$a' : r = (\bar{1}00) : (\bar{1}01) =$	56	54	56 54
$n' : q' = (\bar{1}\bar{1}0) : (01\bar{1}) =$	57	2	56 58
$q' : s' = (01\bar{1}) : (10\bar{1}) =$	53	1	53 10½
$s : m = (10\bar{1}) : (\bar{1}\bar{1}0) =$	69	57	69 51½
$c : m = (001) : (\bar{1}\bar{1}0) =$	79	24	79 30
$b : q' = (010) : (01\bar{1}) =$	50	22	50 22
$q' : c = (01\bar{1}) : (00\bar{1}) =$	40	38	40 38
$a : q = (100) : (01\bar{1}) =$	84	32	84 23
$c' : s' = (00\bar{1}) : (10\bar{1}) =$	47	20	47 19
$c' : t' = (00\bar{1}) : (30\bar{2}) =$	65	28	65 36
$a : t' = (30\bar{2}) : (100) =$	38	45	38 37

No distinct cleavability was observed.

On $\{100\}$ the direction of the plane of the optical axes includes 24° with the c -axis; one of the branches of the hyperbola can be seen at the border of the field of the microscope. Strongly dichroitic: orange and yellow.

§ 4. Crystalform of racemic $\left\{ \text{Co}_{\text{(Eine)}_2}^{(\alpha\text{-Phen})} \right\}_2 (\text{SO}_4)_3 + 12 \text{H}_2\text{O}$.

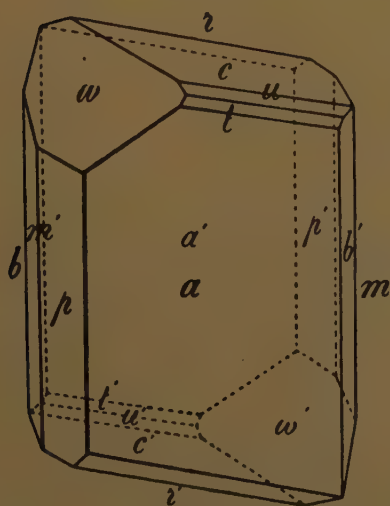


Fig. 3.

This compound crystallizes from its aqueous solution in flat, pale brown and very lustrous crystals, which have quadratic or hexagonal limits. (Fig. 3).

Triclinic-pinacoidal.

$$a : b : c = 1,4062 : 1 : 0,7362;$$

$$A = 101^\circ 15'; \alpha = 93^\circ 19'.$$

$$B = 51 \ 33; \beta = 52 \ 51.$$

$$C = 75 \ 56; \gamma = 80 \ 53.$$

Forms observed: $a = \{100\}$, large and lustrous; $b = \{010\}$, narrower than $c = \{001\}$, both yielding very sharp images; $m = \{110\}$

and $p = \{1\bar{1}0\}$, also very lustrous, p ordinarily narrower than m ; $r = \{\bar{2}01\}$, well developed, yielding good reflections, mostly with only one face present; $s = \{\bar{3}01\}$, narrow, but well measurable; $\omega = \{1\bar{1}1\}$, large and well reflecting; sometimes also: $t = \{201\}$, very narrow, just as: $u = \{101\}$. The habitus is tabular parallel to $\{100\}$, and almost equally developed in the directions of b - and c -axis.

Angular values : Observed : Calculated :

$a:c = (100):(001) =$	$*128^\circ$	27'	—
$a:b' = (100):(0\bar{1}0) =$	$*75$	56	—
$c:b' = (001):(0\bar{1}0) =$	$*101$	15	—
$b':p = (0\bar{1}0):(1\bar{1}0) =$	$*35$	23	—
$b':\omega = (0\bar{1}0):(1\bar{1}1) =$	$*56$	6	—
$a:\omega = (100):(1\bar{1}1) =$	86	$47\frac{1}{2}$	86° $51\frac{1}{2}$
$\omega:p = (1\bar{1}1):(1\bar{1}0) =$	66	2	66 $1\frac{1}{2}$
$\omega:c = (1\bar{1}1):(001) =$	54	6	54 7
$c:p = (001):(1\bar{1}0) =$	59	52	59 $51\frac{1}{2}$
$c:r = (001):(\bar{2}01) =$	26	23	26 $34\frac{1}{2}$
$a':r = (\bar{1}00):(\bar{2}01) =$	25	10	24 $58\frac{1}{2}$
$c:s = (001):(\bar{3}01) =$	32	5	32 2
$s:a' = (\bar{3}01):(\bar{1}00) =$	19	28	19 31
$m:c = (110):(001) =$	72	5	72 5
$a:p = (100):(1\bar{1}0) =$	40	36	40 33
$m:b = (110):(010) =$	47	35	47 $47\frac{1}{2}$
$m:a = (110):(100) =$	56	29	56 $16\frac{1}{2}$
$m:\omega = (1\bar{1}0):(1\bar{1}1) =$	63	47	63 25
$a:t = (100):(201) =$	60	5	60 0
$t:u = (201):(101) =$	36	43	36 39
$u:c = (101):(001) =$	31	39	31 48

A distinct cleavage was not found.

The direction of the plane of the optical axes on $\{100\}$ is almost parallel to the c -axis. On $\{100\}$ one of the branches of the hyperbola is visible in convergent polarized light. No appreciable dichroism is present.

The water-content was found to be: 17,5 %; calculated: 17,6 % H_2O .

§ 5. Crystalform of racemic $\left. \begin{matrix} Co^{(a-Phen)} \\ Co^{(Eine)_2} \end{matrix} \right\} (ClO_3)_3 + 1H_2O$.

From an aqueous solution this salt is deposited in the form of dark

brown thin prisms, which show a great number of faces. (Fig. 4).

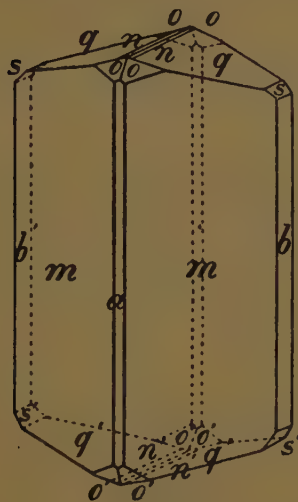


Fig. 4.

Rhombic-bipyramidal.

$$a : b : c = 0,6538 : 1 : 0,2936.$$

Forms observed: $m = \{110\}$, large and lustrous; $q = \{011\}$, well developed and giving sharp reflections; $o = \{211\}$, smaller than q , often dull; $b = \{010\}$, very narrow, but yielding sharp images; $a = \{100\}$, mostly absent, sometimes present with only a single face and dull; $s = \{031\}$, small, but giving clear, somewhat faint images; $n = \{012\}$ and $p = \{150\}$, scarcely visible, yielding only very faint reflections. The habit is elongated in the direction of the c -axis.

Angular values:

Observed: Calculated:

$m : b = (110) : (010) =^*$	56°	49½'	—
$m : q = (110) : (011) =^*$	81	8	—
$b : q = (010) : (011) =$	73	28	73° 38½
$q : q = (011) : (0\bar{1}1) =$	33	6	32 43½
$b : s = (010) : (031) =$	48	33	48 38
$s : q = (031) : (011) =$	25	9	25 5½
$q : n = (011) : (012) =$	8	7	8 0½
$n : n = (012) : (0\bar{1}2) =$	16	50	16 42
$m : o = (110) : (211) =$	48	37	48 27
$o : q = (211) : (0\bar{1}1) =$	50	15	50 25
$a : m = (100) : (110) =$	33	10½	33 10½
$b : p = (010) : (150) =$	17	7	17 0½
$p : m = (150) : (110) =$	39	42	39 49½
$o : q = (211) : (011) =$	40	50	40 45½
$m : o = (110) : (2\bar{1}1) =$	64	36	64 33

Cleavable parallel to q .

On m normally orientated extinction. No axial image was observed. The water-content was determined as: 3 %; calculated: 2,89 % H_2O .

§ 6. It is characteristic that the replacement of one molecule *ethylene-diamine* in the complex *Triethylenediamine-Cobaltic-ion* by one molecule of another bivalent base appears in general to lower the degree of symmetry of the crystalforms of these compounds in an appreciable degree, as becomes evident by comparison of the crystalforms mentioned above with those of the corresponding *Triethylenediamine-Cobaltic-derivatives*. Indeed, by such a substitution the symmetry of the complex

ion, originally consisting in the presence of a ternary and three binary axes, is reduced to that characterized by the presence of a single binary axis¹⁾. However, the new ion remains, as the original one, merely *axially-symmetrical*, and for this reason it will possibly exist in two non-superposable mirror-configurations.

It was tried to separate both these enantiomorphous forms of the compound: 1^o. by means of the *d*-tartrate; 2^o. by the aid of the *bromo-d-camphorsulphonate*. Both these compounds were prepared, starting from the *bromide*, by means of the calculated quantity of *silver-d-tartrate*, respectively *silver-d-bromo-camphorsulphonate*. The two salts thus obtained, crystallized very well. The *d-tartrate* shows in solutions only a slight rotation, which totally depends on the *d-tartaric acid*, which the salt contains; this is also evident from the fact, that the rotatory dispersion appeared to be only weak and of quite normal character. Also the *iodide* obtained from this *tartrate* by precipitation with *NaI*, was proved to be completely *inactive*. Evidently only the *α-tartrate* of the *racemic* ion is present here; its crystalform is described in the following.

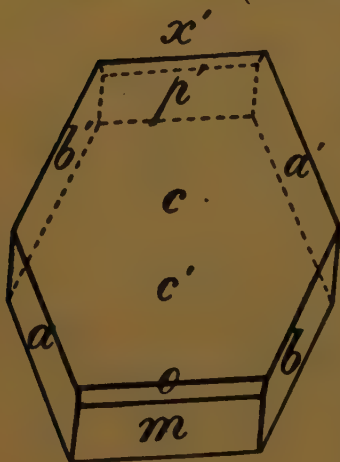
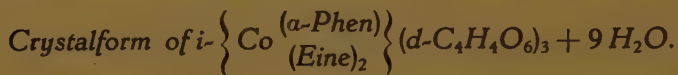


Fig. 5.

This salt crystallizes from water in thin hexagonal plates of a brownish-yellow colour. They are well built and show very lustrous facets (Fig. 5).

Triclinic-pedial.

$$a : b : c = 1,1249 : 1 : 0,9207;$$

$$A = 101^\circ 30\frac{1}{2}'; a = 125^\circ 57'.$$

$$B = 105 \ 58 \ ; \ \beta = 127 \ 25.$$

$$C = 44 \ 30\frac{1}{2} \ ; \ \gamma = 35 \ 23.$$

Forms observed: $c = \{001\}$ and $c' = \{00\bar{1}\}$, large and highly lustrous; $a = \{100\}$, $a' = \{100\}$, $b = \{010\}$, and $b' = \{0\bar{1}0\}$, all about equally well developed and giving excellent reflections; $m = \{110\}$ and $p' = \{1\bar{1}0\}$, well developed

and lustrous; $x = \{11\bar{1}\}$, large and giving sharp images; $x' = \{1\bar{1}1\}$, narrow and somewhat duller; $o = \{111\}$, very narrow and yielding faint images only. The habit of the crystals is thin tabular parallel to $\{001\}$, often with elongation parallel to the edge $c : m$.

Angular values:

Observed : Calculated :

$$a : b = (100) : (010) = *135^\circ \ 29\frac{1}{2}' \quad -$$

$$b : c = (010) : (001) = *78 \ 29\frac{1}{2}' \quad -$$

$$a : c = (100) : (001) = *74 \ 2 \quad -$$

¹⁾ This axis is polar and connects the centre of the α -Phenanthroline-molecule with the midd of the opposite edge of the octahedron.

Angular values : Observed : Calculated :

$a : m = (100) : (110) =$	*77	13	—	
$c' : x = (00\bar{1}) : (11\bar{1}) =$	*58	13	—	
$a : x = (100) : (11\bar{1}) =$	95	5	95°	1 $\frac{1}{2}$ '
$b : x = (010) : (11\bar{1}) =$	70	33	70	49
$b : m = (010) : (110) =$	58	16 $\frac{1}{2}$	58	16 $\frac{1}{2}$
$c : o = (001) : (111) =$	25	5	24	48
$o : m = (111) : (110) =$	27	21	27	31
$c : m = (001) : (110) =$	52	26	52	19
$m : x = (110) : (11\bar{1}) =$	69	21	69	28

No distinct cleavage was observed.

The direction of the optical axial plane on {001} includes an angle of 6° with the edge $c : o$. The crystals are only unappreciably dichroitic.

The water-content was: 11,9 %; calculated: 11,8 % H_2O .

§ 7. On the other hand the *d*-bromocamphorsulphonate mentioned before appeared to manifest only a weak rotation of its solution for Na-light; but this proved to be appreciably greater for smaller wave-lengths, while also the rotatory dispersion appeared to be distinctly abnormal, with a COTTON-effect in the vicinity of an absorption-band in the blue-violet part of the spectrum. Later it was proved, moreover, that the iodide prepared from this *d*-bromocamphorsulphonate by means of NaI, was indeed appreciably active in solution; more particularly, it was proved to be the salt of the levogyrotory ion. Tentatives to execute the fission into optical antipodes by means of sodium- α -camphornitronate gave hitherto no positive results.

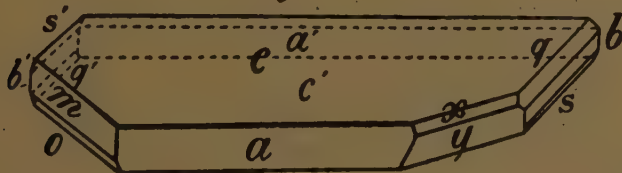
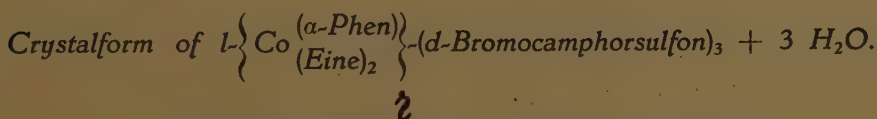


Fig. 6.

Very thin, orange or yellow, often badly built crystalplates (Fig. 6).

Triclinic-pedial.

$$a : b : c = 1,2356 : 1 : 2,1156.$$

$$A = 82^\circ 8'; \alpha = 82^\circ 22'.$$

$$B = 103 38; \beta = 103 30\frac{1}{2}.$$

$$C = 88 9; \gamma = 89 58.$$

Forms observed: $c = \{001\}$ and $c' = \{00\bar{1}\}$, both predominant and yielding very sharp reflections; $a = \{100\}$ and $a' = \{\bar{1}00\}$, well developed and very lustrous; $b = \{010\}$, narrow, well measurable; $q = \{011\}$, narrow, giving only faint images; $s = \{01\bar{1}\}$, broader and well reflecting; the corresponding forms: $b' = \{010\}$, $q' = \{0\bar{1}1\}$ and $s' = \{0\bar{1}\bar{1}\}$ are mostly absent or are scarcely visible; $r = \{\bar{1}01\}$, well developed and yielding sharp reflexes; $m = \{\bar{1}10\}$, rather broad, dull; $o = \{\bar{1}\bar{1}\bar{1}\}$, narrower than m , but reflecting a little better; $x = \{221\}$, narrow, but well measurable; $y = \{11\bar{1}\}$, broader than x and excellently reflecting. The habitus is thin tabular parallel to $\{001\}$, with an elongation in the direction of the b -axis. The angles vary commonly within rather wide limits.

<i>Angular values:</i>	<i>Observed:</i>	<i>Calculated:</i>	
$c:a = (001):(100) =$	$^{\circ}76$	22'	—
$c:b = (001):(010) =$	$^{\circ}97$	52	—
$c:r = (001):(\bar{1}01) =$	$^{\circ}70$	1	—
$q:c = (011):(001) =$	$^{\circ}70$	33	—
$c:s = (001):(01\bar{1}) =$	$^{\circ}57$	50	—
$a:q = (100):(011) =$	85	56	$^{\circ}86$ 26'
$b:q = (010):(011) =$	26	58	27 19
$b:s = (010):(01\bar{1}) =$	24	22	24 18
$c:x = (001):(221) =$	76	58	77 14
$x:y = (221):(11\bar{1}) =$	31	29	31 $8\frac{1}{2}$
$c':y = (00\bar{1}):(11\bar{1}) =$	71	27	71 37
$c:m = (001):(\bar{1}\bar{1}0) =$	75	26	75 28
$m:o = (\bar{1}\bar{1}0):(\bar{1}\bar{1}\bar{1}) =$	21	2	21 51
$c':o = (00\bar{1}):(\bar{1}\bar{1}\bar{1}) =$	83	0	82 41
$a:y = (100):(11\bar{1}) =$	60	3	60 30
$y:s = (11\bar{1}):(01\bar{1}) =$	36	37	36 47
$a':s = (\bar{1}00):(01\bar{1}) =$	82	21	82 43
$a:m = (100):(\bar{1}\bar{1}0) =$	39	43	39 50
$a:o = (100):(\bar{1}\bar{1}\bar{1}) =$	42	55	42 49
$a:x = (100):(221) =$	50	5	50 37

No distinct cleavage was stated.

On $\{001\}$ the extinction is practically parallel, respectively perpendicular to the edge $c:r$; the plane of the optical axes is parallel to $\{010\}$. Only slightly dichroitic: orange and orange-yellow.

The determination of the water-content gave: 3.87 % H_2O ; calculated: 3.93 % for 3 H_2O .

§ 8. The possibility of a fission of the complex ion by means of the *d*-bromocamphorsulphonates thus being demonstrated, the fission considered

was started now in a systematical way and trials were made to isolate the pure dextro- and levogyrotory components by the aid of fractional crystallisation.

We started always with the racemic *bromide*, prepared from the solution of the corresponding *iodide* by treating this with freshly precipitated and washed *silverbromide*; the *bromide* thus obtained was several times recrystallized from water. By adding pure *silver-d-bromocamphorsulphonate* ($+ 1\frac{1}{2} H_2O$) in the calculated quantity to its solution and by heating it on the waterbath, after filtration a clear orange-yellow solution is obtained, which after evaporation on the waterbath and after cooling yields a pale, salmon-coloured salt as principal product, crystallizing in small, lustrous tables. The mother-liquor deposits, after being kept for some time at roomtemperature, pale yellow flat needles or small tables; in this way in total six fractions were separated, until finally the last mother-liquor solidifies into a soft, almost resinous, pale orange-coloured mass, in which again some spare small crystals are included, which were eliminated from it by means of a pincet.

The first fraction appeared to be the *d-bromocamphorsulphonate* of the *levogyrotory* ion, already mentioned before; the last fraction, after conversion into the *iodide*, appeared to yield a mixture, consisting principally of the corresponding derivative of the *dextrogyrotary* ion, accompanied by a small quantity of the racemic *iodide*. The second fraction was the same as the first, its rotatory power being, however, somewhat lessened by the admixture of a little quantity of the salt of the *dextrogyrotory* component; the third and fourth fractions were only feebly levogyrotory and gave, after conversion into the *iodide*, chiefly the optically inactive salt. The fifth fraction was strongly dextrogyrotory; after conversion into the *iodide* this appeared also to be dextrogyrotory, but with admixture of an appreciable quantity of the racemic salt. From these data it becomes obvious that the fission by means of the *d-bromocamphorsulphonic acid* goes on in such a way, that first the less soluble *d-bromocamphorsulphonic* of the *levogyrotory* ion is deposited: the corresponding salt of the *dextrogyrotory* ion is far more soluble and is found accumulated principally in the last mother-liquids, which crystallize with difficulty. Both the optically-active *iodide*, separated from the *d-bromocamphorsulphonates* by means of *NaI*, appeared to be far more soluble than the racemic *iodide*: a fact making it possible to free the active iodides for the greater part from admixed racemic *iodide*. The greater solubility of the optically-active salts in comparison with that of the racemic compounds is in full agreement with the fact, that under ordinary circumstances the antipodes are really metastable with respect to the racemic compound. It is remarkable, that the racemic *iodide* possesses a somewhat deeper, more orange- or reddish-tinged colour than the more pale orange-coloured optically-active *iodides*; the same holds for their solutions. The rotations and rotatory dispersions

Observed, specific and molecular Rotations of the Solutions of anhydrous $l-\left\{ \text{Co} \begin{matrix} (\alpha\text{-Phen}) \\ (\text{Eine})_2 \end{matrix} \right\}-(d\text{-bromocamphorsulphon.})_3$			
The solution contained 0,4136 gramme of salt, i.e. 0,3975 gramme of the anhydrous substance in 100 ccm. solution. Length of the tube: 1 dm.			
Wave-length λ in A. U.:	Rotation α observed:	Specific Rotation $[\alpha]$:	Molecular Rotation $[M]$:
6850 tot 6258	+ 0.17 ⁻	+ 42.8	+ 564.1
6090	+ 0.13 ⁻	+ 32.7	+ 431.4
5940	+ 0.07 ⁺	+ 17.7	+ 234.1
5655	- 0.08	- 20.1	- 265.4
5600	- 0.13 ⁺	- 32.8	- 432.0
5540	- 0.20	- 50.3	- 663.5
5470	- 0.31 ⁻	- 78.0	- 1028
5435	- 0.37	- 93.1	- 1228
5330	- 0.54 ⁺	- 135.8	- 1792
5240	- 0.72 ⁻	- 181.1	- 2389
5198	- 0.73	- 183.7	- 2422
5160	- 0.72 ⁻	- 181.1	- 2389
5080	- 0.60 ⁻	- 150.9	- 1991
5070	- 0.55 ⁻	- 138.4	- 1825
5030	- 0.10	- 25.1	- 331.8
5010	- 0.21 ⁺	+ 52.8	+ 696.8

observed are reviewed in the accompanying tables; Fig. 7, moreover, gives a graphical representation of these numbers.

The specific rotation becomes equal to zero for a wave-length of 5025 A.U.; from Fig. 7 the shift of the curve with respect to the corresponding curve of the *iodide* may be seen, as a consequence of the rotatory influence of the *dextrogyratory bromocamphorsulphonic acid* contained in it.

In the case of the *dextrogyratory antipode*, the measurements were made only between 5140 and 6290 A.U., as a consequence of the greater concentration used here. The part of the dispersion-curve determined, however, proves convincingly, that the curve is completely analogous to that of the *levogyrotary component*, being its mirror-image.

The curve of the rotatory dispersion in the case of the *iodide* is also

Observed, specific and molecular Rotations of the Solutions of levogyrotory $\left\{ \begin{array}{l} \text{Co } (\alpha\text{-Phen}) \\ (\text{Eine})_2 \end{array} \right\} \text{I}_3$.			
The solution contained 0.1230 gram iodide in 100 ccm. solution. The length of the tube was: 1 dm.			
Wave-length in A. U.:	Rotation α observed:	Specific Rotation $[\alpha]$:	Molecular Rotation $[M]$:
6850	— 0.02^+	— 16.3	— 124.2
6445	— 0.01^4	— 11.4	— 87.0
6258	— 0.01^3	— 10.6	— 80.7
6092	— 0.02	— 16.3	— 124.2
5940	— 0.04^-	— 32.5	— 248.5
5783	— 0.08^-	— 65.0	— 497.0
5655	— 0.14	— 113.8	— 869.6
5540	— 0.20	— 162.6	— 1242.3
5435	— 0.29	— 235.1	— 1801.3
5330	— 0.39	— 317.0	— 2422.4
5240	— 0.48	— 389.9	— 2981.4
5160	— 0.52	— 422.8	— 3230
5070	— 0.48^-	— 388.8	— 2981.4
5005	— 0.33	— 268.3	— 2050
4935	— 0.07^-	— 56.9	— 434.8
4865	+ 0.23	+ 186.9	+ 1429
4830	+ 0.58	+ 471.6	+ 3603
4755	+ 0.82	+ 666.8	+ 5093
4635	+ 0.97	+ 788.6	+ 6025

typically abnormal: between 4635 and 4910 A.U. the solutions are dextro- (or levo-)rotatory for the smaller wave-lengths, levo- (resp. dextro-)gyrotory for the greater wave-lengths. The rotation becomes zero for $\lambda=4910$ A.U.; a COTTON-effect is present, as can be seen immediately from the curve in Fig. 7. The maximum specific rotation is in the case of the levogyrotory antipode situated in the vicinity of 4500 A.U. and has the value of about $+840^\circ$, while the greatest levo-rotation, occurring at 5160 A.U. is numerically only half this value, i.e. -426° .

Although this dispersion-curve is not determined in its full extension,

Observed specific and molecular Rotations of a Solution of dextrogyratory $\left\{ \begin{array}{c} \text{Co } (\alpha\text{-Phen}) \\ (\text{Eine})_2 \end{array} \right\} \text{I}_3$			
The solution contained 0,2700 gramme of the salt in 100 ccm. of the solution. The length of the tube is 1 dm.			
Wave-lengths in A. U.:	Rotation α observed:	Specific Rotation $[\alpha]$:	Molecular Rotation $[M]$:
6290	0.03	+ 11.1	+ 84.9
6090	0.05	+ 18.5	+ 141.5
5940	0.09	+ 33.3	+ 254.7
5783	0.18	+ 66.8	+ 509.4
5655	0.31	+ 114.8	+ 877.2
5540	0.45+	+ 166.8	+ 1273
5435	0.61	+ 225.9	+ 1726
5330	0.84	+ 311.1	+ 2377
5240	1.04	+ 385.2	+ 2943
5160	1.16	+ 429.6	+ 3282
5140	1.13+	+ 418.5	+ 3197

there is no doubt about the fact, that it is in Fig. 7 the mirror-image of the first one, the almost pure component therefore really being present here.

For the purpose of comparison, the dispersion-curve for *d*- (or *l*-) *Triethylenediamine-Cobaltic-iodide*¹⁾ is also drawn in Fig. 7. This comparison shows that the substitution of one of the molecules $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$ in the complex ion by one molecule of the also symmetrically built molecule of α -Phenanthroline has the result that, notwithstanding the general character of the original dispersion-curve is preserved, there is a slight shift of the zero-rotation from 4845 A. U. towards 4910 A.U., besides an increase of both rotation-maxima, which, moreover, are shifted in opposite directions: the one maximum being shifted from 4735 A.U. and a value of $412^\circ.5$ towards 4500 A.U. approximately and a value of 840° , while the other is moved from 5100 A.U. and 406° towards 5160 A.U. and 426° . The latter change is, however, insignificant in comparison with that of the other maximum, as a consequence of which the originally almost symmetrical dispersion-curve of

¹⁾ The new measurements of the values necessary for the construction of the curve in Fig. 7, were made by my former assistant, Mr. P. KOETS.

the highly symmetrical Triethylenediamine-Cobalti-complex is now distorted into a distinctly unsymmetrical curve. The substitution within the complex ion influences therefore chiefly the first rotation-maximum, corresponding to the shorter wave-lengths; on the contrary, the second

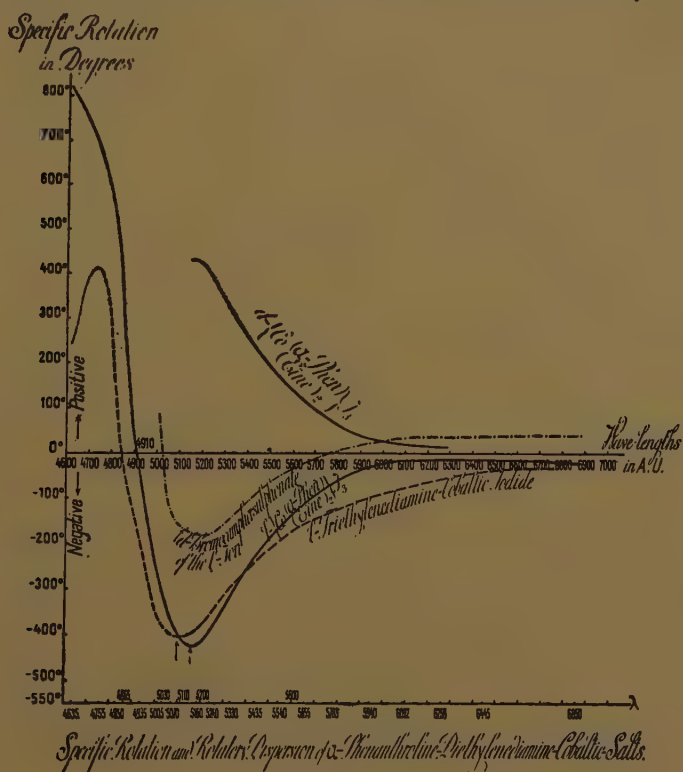


Fig. 7.

maximum, as well as the zero-point of the curve are evidently influenced only to an unappreciable extent.

§ 9. Several tentatives were made also to obtain the optically-active salts or their derivatives in a well crystallized form, with the purpose to control with these crystals the validity of PASTEUR's law concerning the relation between optical activity and enantiomorphism of crystalline forms also in this case; moreover, after isolation of the enantiomorphous individuals it would then be possible to determine the specific rotation in solution once more. For the isolation of the completely pure optically-active *iodides* is always somewhat difficult, because these iodides were not obtainable in good individual crystals, so that no absolute certainty existed, that no trace of admixed racemic iodide made the rotation appear too low. With respect to the formerly observed crystallizing power of the racemic *chlorate*, the choice was first of all fixed upon the optically-active *chlorates* for this purpose; later also the *sulphates* and the *perchlorates* were prepared. The different optically-active fractions of

the *iodides*, therefore, were converted into the corresponding *chlorates*, *sulphates* or *perchlorates* by means of the *silver-salts* of these acids, and the solutions thus obtained were allowed to crystallize very slowly during evaporation at room-temperature. Soon it became clear, however, that it was much more difficult to obtain good, measurable crystals of these active salts, than such was the case with the racemic substances, as a consequence of the much greater solubility of the first. Of the *sulphate* hitherto no measurable crystals could be obtained; the *perchlorates* crystallize badly, but it could be stated, that they were triclinic-pedial.



From an aqueous solution this salt is deposited in the shape of very small, orange-yellow needles or short, rectangularly bordered prisms, which evidently contain $2 \text{H}_2\text{O}$ ($=5.4\%$).

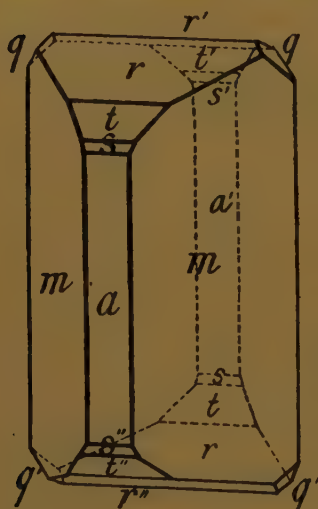


Fig. 8.

Monoclinic; probably *sphenoidal* and pseudo-rhombic.

$$a : b : c = 1,5133 : 1 : 0,4433;$$

$$\beta = 87^\circ 55'.$$

Forms observed: $m = \{110\}$, well developed and strongly lustrous; $a = \{100\}$, commonly narrower than m , excellently reflecting, often its faces developed equally in height and in breadth as highly developed faces, m in that case being much narrower; $r = \{101\}$ and $r' = \{101\}$, almost equally broad and yielding good reflections; $t = \{301\}$ and $t' = \{301\}$, narrower than r , but giving sharp images; $s = \{501\}$ and $s' = \{501\}$, much narrower than r and t , but reflecting very well; $q = \{031\}$, often

absent, sometimes observable as small truncation of the ends of the prismatic crystals and only approximately measurable. The habit is long-prismatic parallel to the c -axis or shorter, with flattening parallel to $\{100\}$. (Fig. 8).

Angular values :

Observed : Calculated :

$a : m = (100) : (110) =^*$	56°	31½'	—
$a' : s' = (\bar{1}00) : (\bar{5}01) =^*$	34	59	—
$a' : r' = (\bar{1}00) : (\bar{1}01) =^*$	75	36	—
$s' : r' = (\bar{5}01) : (\bar{1}01) =$	40	35	40° 37'
$r' : r = (\bar{1}01) : (101) =$	32	38	32 38½
$r : s = (101) : (501) =$	37	36	38 6½
$a : s = (100) : (501) =$	34	8	33 39

Angular values :

Observed : Calculated :

$a' : t = (\bar{1}00) : (\bar{3}0\bar{1}) =$	47	37	47	31
$m : q = (110) : (031) = ca.$	47°		47	16
$m : m = (110) : (\bar{1}10) =$	66	57	66	57
$m : t = (110) : (301) =$	68	14	68	8
$c : q$ (plane angle) $= ca.$	53°		53	2½

No distinct cleavage was observed.

On {100} there is in no situation complete extinction, as a consequence of a strong conical refraction. Perpendicular to {100} one of the optical axes emerges. The plane of the optical axes is {010}; inclined dispersion. No appreciable dichroism is observable.

§ 11. The production of *Triethylenediamine-Cobaltic*-complexes during the reaction between mono- and bivalent amines in solution on salts of the *Diethylenediamine-chloro-aquo-Cobaltic-ion*, as mentioned above, was also stated in analogous reactions with other mono- and bi-valent amines like those already described; the phenomenon even appeared to occur also, when *Diethylenediamine-dihalogeno-Cobaltic-salts* (*Praseo-salts*) were used in these reactions ¹⁾. Thus e. g. in the reaction between *l-Menthyl-*

amine and the corresponding *chloro-aquo-Cobaltic* salt and after treating the reaction-products with *bariumchloride*, big crystals with the colour of the *Luteo-cobaltic-salts* were obtained, possessing the form of (Fig. 9).

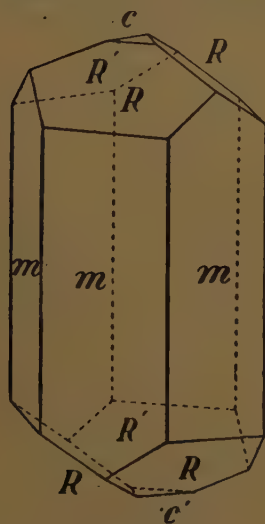


Fig. 9.

Ditrigonal-scalenohedral.

$$a = 107^\circ 34'; a : c = 1 : 0,9758.$$

Forms observed: $m = \{10\bar{1}0\} = \{2\bar{1}1\}$, large and very lustrous; $R = \{10\bar{1}1\} = \{100\}$, well developed and yielding good images; $c = \{0001\} = \{111\}$, also well developed and sharply reflecting. The crystals are often peculiarly distorted and tabular parallel to faces of m .

Angular values :

Observed : Calculated :

$c : R = (0001) : (10\bar{1}1) =$	*87°	58'	—
$R : R = (10\bar{1}1) : (\bar{1}101) =$	64	29	64° 23'
$m : R = (10\bar{1}0) : (10\bar{1}1) =$	52	2	52 2
$m : R = (0\bar{1}10) : (10\bar{1}1) =$	72	6	72 5
$m : m = (10\bar{1}0) : (0\bar{1}10) =$	59	58	60 0

¹⁾ Comp.: F. M. JAEGER and P. KOETS, These Proceed. 29, (1926), p. 67.

On *m* distinctly dichroitic: for vibrations parallel to the *c*-axis pale orange-red, for those perpendicular to them: orange. Optically-uniaxial without circular polarisation; negative. Notwithstanding the deviating habit, these crystals are identical with those of $\{\text{Co}(\text{Eine})_3\} \text{Cl}_3 + 3 \text{H}_2\text{O}$, formerly described¹⁾. The determinations of H_2O and Cl were also in full agreement with this constitution, no doubt whatsoever being possible with respect to the said identity.

§ 12. The same fact was stated with respect to the *Chlorosulphates*, which are produced, if racemic or levoçyrotory *Pentane-2-4-diamine* or the corresponding *meto*-base are heated with the *chloro-aquo-salts* in aqueous solution in sealed glass-tubes at 110°C . during six hours. In this case there is deposited a salt of typically rhombohedral form (Fig. 10), as described here.

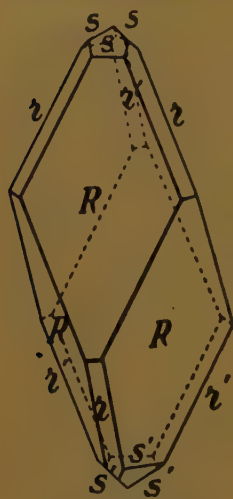


Fig. 10.

Ditrigonal-scalenohedral.

$$\alpha = 50^\circ 36'; a : c = 1 : 3.0544.$$

Forms observed: $R = \{100\} = \{10\bar{1}1\}$, strongly predominant and well reflecting; $r = \{110\} = \{011\bar{2}\}$, as narrow truncation of the polar edges of R , yielding mostly faint, rarely also sharper reflections; $s = \{211\} = \{\bar{1}014\}$, small, but well measurable.

Angular values :	Observed :	Calculated :
$s : s' = (211) : (121) = 69^\circ 53'$		—
$R : R = (100) : (0\bar{1}0) = 67^\circ 13'$		$67^\circ 9'$
$R : r = (100) : (110) = 56^\circ 23\frac{1}{2}'$		$56^\circ 25\frac{1}{2}'$

No distinct cleavage was present.

Optically-uniaxial; negative, without circular polarisation.

§ 13. The optically-active *Pentane-2-4-diamines* necessary for these experiments were obtained from the racemic base by means of the *acid d-tartrates*. To a solution of the racemic base, the strength of which was carefully determined, a solution of dextrogyrotory *tartaric acid* was added in proportion of 2 molecules of the acid to 1 molecule of the base. When the solution is sufficiently concentrated on the waterbath, crystallization sets in; during the evaporation on the waterbath a certain quantity of *acetone* is added to the solution, by which evidently the evaporation of the base set free by a slow dissociation of the *bitartrate*, is somewhat retarded (KOETS), while also the solubility of the *bitartrate* in a mixture of water and acetone is less than in water alone. After recrystallization

¹⁾ F. M. JAEGER, Rec. d. Trav. Chim. d. Pays-Bas, loco cit.

stallizing twelve times, the specific rotation of the salt appeared to remain constant: $[a]_D = +26^\circ$.

Analysis: 5.07 m.G. give 0.304 ccm. N_2 of $16^\circ C$. and a pressure of 763 mm.; this corresponds to 7.11 % N, while 6.97 % N is calculated.

After the *tartaric acid* is eliminated by means of *KCl*, the base was set free from the hydrochloride obtained by means of solid *KOH*; the less soluble *bitartrate* gives in this way the *levo*-gyratory base.

Crystalform of l-Pentane-2-4-diamine-bi-d-tartrate: $C_5H_{10}(NH_2)_2, 2C_4O_6H_6$.

This substance crystallizes in small, transparent, colourless and highly lustrous crystals of varying habitus. From warm solutions individuals are deposited having the shape of Fig. 11a. From cold solutions, however, the crystals of Fig. 11b and 11c are deposited, which apparently do not show any trace of hemihedrism. The vertical zone is only approximately measurable, because of a fine striation of the already very narrow faces, so that multiple reflections occur.

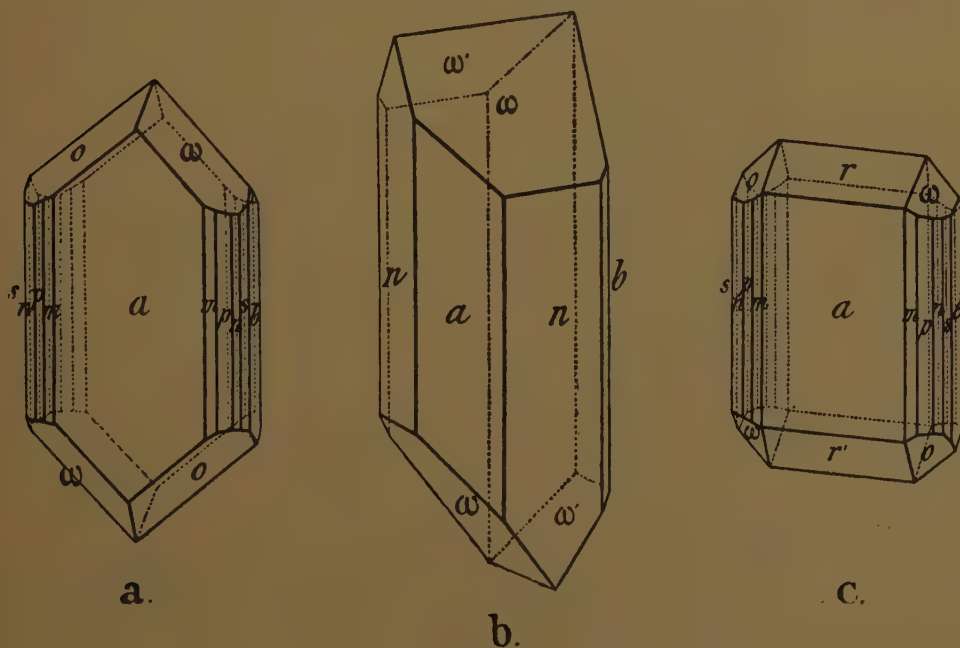


Fig. 11.

Rhombic-bisphenoidal.

$$a : b : c = 1.3518 : 1 : 0.9750.$$

Forms observed: $a = \{100\}$, mostly broadest of all, rarely narrower, however, than $n = \{110\}$; when all prisms are present, $n = \{110\}$, $m = \{310\}$ and $p = \{210\}$, are all almost equally broad and highly lustrous; $s = \{140\}$ and $b = \{110\}$, however, are very narrow and dull; these forms

are often absent. Furthermore: $\omega = \{111\}$ and $o = \{\bar{1}\bar{1}1\}$, mostly equally well developed and physically only unappreciably different, both yielding sharp images. Sometimes only $\omega = \{111\}$ is present as a typical bisphenoid. Further: $r = \{101\}$ and $t = \{701\}$, rarely present otherwise than with crystals of type 11c, but in that case large and very lustrous; $q = \{011\}$, well developed, often absent, but always yielding good reflections; $c = \{001\}$, mostly absent and extremely narrow.

Angular values : Observed : Calculated :

$\omega : o = (111) : (\bar{1}\bar{1}1) =$	$^{\circ}77$	$26\frac{1}{2}$	—	
$a : \omega = (100) : (111) =$	$^{\circ}63$	$38\frac{1}{2}$	—	
$\omega : o = (111) : (\bar{1}\bar{1}1) =$	52	43	52°	$43'$
$m : \omega = (310) : (111) =$	48	35	48	34
$\omega : b = (111) : (010) =$	51	17	51	17
$a : m = (100) : (310) =$	24	15	24	$15\frac{1}{2}$
$m : p = (310) : (210) =$	9	44	9	48
$p : n = (210) : (110) =$	19	30	19	27
$n : s = (110) : (140) =$	23	51	23	$42\frac{1}{2}$
$s : b = (140) : (010) =$	12	35	12	47
$n : n = (110) : (\bar{1}\bar{1}0) =$	73	2	72	59
$a : n = (100) : (110) =$	53	31	53	31
$n : \omega = (110) : (111) =$	40	39	40	$40\frac{1}{2}$
$\omega : \omega = (111) : (\bar{1}\bar{1}1) =$	98	42	98	39
$n : \omega = (110) : (\bar{1}\bar{1}1) =$	76	31	76	$36\frac{1}{2}$
$\omega : q = (111) : (011) =$	26	$18\frac{1}{2}$	26	15
$\omega : \omega = (111) : (\bar{1}\bar{1}1) =$	128	47	128	43
$r : \omega = (101) : (111) =$	38	47	38	43
$r : o = (101) : (\bar{1}\bar{1}1) =$	73	59	73	48
$r : r = (101) : (\bar{1}01) =$	69	20	69	22
$r : t = (101) : (201) =$	19	42	20	35

No distinct cleavability was found.

On $\{100\}$ and in the zone of the c-axis everywhere normal extinction.

The plane of the optical axes is $\{001\}$; on $\{100\}$ both branches of the hyperbola are visible in convergent polarized light.

§ 14. On using now this *l*-Pentane-2-4-diamine in the fore-said experiments, also crystals were met with, which showed only $R = \{100\}$ or only R and c combined; if the *meso*-base was used, crystals were found, which showed R , r and s . But in both cases the angular values were completely analogous. As already mentioned above, the same crystal-forms were met with in the case, that α -Phenanthroline reacts with the chloro-aquo-salt; they are all identical with those of the chlorosulphate

of the *Triethylenediamine-Cobaltic-ion*, which salt has a constitution represented by the formula: $\left\{ \text{Co} (\text{Eine})_3 \right\} \left(\text{SO}_4 \right)^{\text{Cl}} + n\text{H}_2\text{O}$, in which n is most probably equal to 3. Analysis gave no quite reliable results, probably as a consequence of a partial decomposition of the salt on heating or by the admixture of accessory products (*trichloride* and other *chlorosulphates*), which could not be completely eliminated by recrystallisation.

If all these *chlorosulphates* be converted into the corresponding *iodides* by means of NaI , the salts obtained appear to be all identical, notwithstanding the more or less accidental deviations in their habitus. They all represent the *iodide* of the *Triethylenediamine-Cobaltic-ion*: rhombic-bipyramidal; $a:b:c=0,8538:1:0,8625$ or values only slightly different from this; forms: $o\{111\}$, $c=\{001\}$; $\omega=\{221\}$; $q=\{041\}$; angular values: $c:o=52^\circ56'$ till $53^\circ5'$; $o;o=62^\circ27'$ till $62^\circ48'$; $o:\omega=15^\circ58'$ till $16^\circ11'$; $o:o'=74^\circ39'$ till $75^\circ3'$; etc. Also the optical orientation is in all these cases identical. Their constitution is in all cases: $\{\text{Co}(\text{Eine})_3\} \text{I}_3 + 1\text{H}_2\text{O}$. It is remarkable, that in the last mentioned reactions these *Triethylenediamine-Cobaltic-derivatives* seem to represent indeed the *principal product* of the reaction; the bases used are only present in the last mother-liquids, which do not crystallize very well.

Also if *d-*, *l-*, or *rac. a-Propylenediamine* in aqueous solution react with the *chloro-aquo-salt*, always the same *chlorosulphates*, respectively *iodides* are obtained. If really the normal reaction-products shall be obtained in such cases, the only feasible method consists in the reaction between the *anhydrous* bases (or their monohydrates) and the corresponding *Praseo-salts* at *low* temperatures, a method already followed by PFEIFFER, GRASSMANN and PIETSCH¹⁾ in the case of *a-Propylenediamine*. Indeed, in this way the desired *a-Propylenediamine-diethylenediamine-Cobaltic-salts* were obtained, showing the properties already mentioned by the said authors. However, it was not possible hitherto to obtain these salts in a form, suitable for crystallographical research; in most cases only fine needles grouped in rosettes were obtained in this way.

The investigations of the products obtainable by the reaction between the *anhydrous pentane-diamines* and the *praseo-Cobaltic-salts* are meanwhile continued by us.

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¹⁾ P. PFEIFFER, TH. GRASSMANN and H. PIETSCH, Zeits. f. anorg. Chemie, 58, 301, (1908).

Mathematics. — “On treating Skew Correlation”. (The End). By Prof.
M. J. VAN UVEN. (Communicated by Prof. W. KAPTEYN).

(Communicated at the meeting of January 30, 1926).

Finally we shall consider the most general case, in which r is not equal to r' .

The equation (24), however, is essentially satisfied.

At present we put, in order to obtain formulae analogous to (28):

$$\left. \begin{aligned} z &= r \cos \left(\frac{\omega}{2} + \theta \right) , & z' &= r' \cos \left(\frac{\omega}{2} - \theta \right) , \\ \zeta &= r \sin \left(\frac{\omega}{2} + \theta \right) , & \zeta' &= r' \sin \left(\frac{\omega}{2} - \theta \right) , \end{aligned} \right\} \dots (43)$$

whence

$$A \equiv z z' - \zeta \zeta' = r r' \cos \omega, \dots (44)$$

$$B \equiv z \zeta' + z' \zeta = r r' \sin \omega. \dots (45)$$

So, we have also in this case

$$\operatorname{tg} \omega = \frac{z \zeta' + z' \zeta}{z z' - \zeta \zeta'} = \frac{B}{A} \dots (32)$$

Besides we put

$$r = \frac{R}{\lambda} , \quad r' = \lambda R, \dots (46)$$

whence

$$r r' = R^2 \dots (47)$$

Putting similarly

$$z = \frac{Z}{\lambda} , \quad z' = \lambda Z', \dots (48)$$

we obtain

$$\left. \begin{aligned} Z &= R \cos \left(\frac{\omega}{2} + \theta \right) , & Z' &= R \cos \left(\frac{\omega}{2} - \theta \right) \\ Z^2 - 2 \cos \omega \cdot Z Z' + Z'^2 &= R^2 \sin^2 \omega, \end{aligned} \right\} \dots (49)$$

and

or, putting

$$\begin{aligned} Z &= T \sin \omega , & Z' &= T' \sin \omega , & \cos \omega &= \gamma, \\ T^2 - 2 \gamma T T' + T'^2 &= R^2. \end{aligned}$$

So we have again arrived at the usual unimodular equation. The difference, however, between this and the former cases is, that γ (with ω) is no longer, neither a constant, nor a function only of R , but that γ is a function both of R and θ , λ being too a function of R and θ .

By introducing the mean angle ω and the auxiliar angle τ , we here arrive at a set of variables t and t' :

$$\left. \begin{aligned} t &= \frac{\sin\left(\frac{\omega+\bar{\omega}}{2} + \tau\right)}{\sin \omega \cdot \sin \bar{\omega}} \cdot \lambda z + \frac{\sin\left(\frac{\omega-\bar{\omega}}{2} - \tau\right)}{\sin \omega \cdot \sin \bar{\omega}} \cdot \frac{z'}{\lambda} \\ t' &= \frac{\sin\left(\frac{\omega-\bar{\omega}}{2} + \tau\right)}{\sin \omega \cdot \sin \bar{\omega}} \cdot \lambda z + \frac{\sin\left(\frac{\omega+\bar{\omega}}{2} - \tau\right)}{\sin \omega \cdot \sin \bar{\omega}} \cdot \frac{z'}{\lambda} \end{aligned} \right\} \quad (50)$$

between which there is unimodular linear correlation, the coefficient of correlation being $\gamma = \cos \omega$.

It is true that, by choosing $\tau = \frac{\omega-\bar{\omega}}{2}$, we can free the expression for t from its second term (with z') and bring it into the form

$$t = \frac{\lambda z}{\sin \omega},$$

but here this variable is (on account of the factor λ) no longer a function only of x (as in (42)); and, as a rule, we are no more able, whatever value of τ may be chosen, to free the variable t from its dependence on x' ¹⁾. Therefore:

In the most general case, where an incontestable discrepancy is stated between the value of $r^2 = z^2 + \zeta^2$ and that of $r'^2 = z'^2 + \zeta'^2$ in the different combinations (z_k, z'_i) , it will not even be possible to make one of the variables t, t' into a pure function of x (or of x').

In order to make out, in the case $r = r'$, whether the variability of ω is the effect of the accidental perturbations of a quantity essentially constant, or results from the dependence between ω and r , we must institute a statistic investigation. First—in order to make this dependence more obvious, we shall introduce—as new variables—functions of ω and r ,

¹⁾ By the high degree of indefiniteness in solving the problem proposed we might expect, that, in any case, it would be possible to submit one of the final variables (t, t') to the condition that it be a pure function of only one of the primary variables. Indeed, we may, in a theoretical sense, choose τ as such a function of z and z' that $\frac{\partial t}{\partial z'} = 0$ is satisfied.

Apart from the difficulties arising in solving the resulting differential equation for τ , the solution based upon this choice of τ will lose so much of its practical importance that we safely may leave it out of consideration.

which have a variation domain as large as possible. We shall also replace r , not being exactly equal to the corresponding r' , by $R = \sqrt{rr'}$. So we choose as new variables: $L = \log R$ and $M = \operatorname{tg} \omega$. Both these functions can vary from $-\infty$ to $+\infty$. Representing each pair (r, ω) by a point having the coordinates L, M , a relation, not too intricate, between r and ω will reveal itself as a not too capriciously curved (eventually straight) line, which can be drawn through the points (L, M) .

In consequence of inevitable accidental perturbations, the empirically given points (L, M) will be grouped, more or less closely, round a certain line. Here two cases are to be distinguished:

1. If the points (L, M) are rather closely round a straight line $M = M_0$ ($= \text{const.}$), we may then conclude that M (thus also ω) is really constant.
2. If, on the contrary, the points (L, M) are within a rather narrow domain round another straight line, or round a curved line, we may then consider the equation $M = F(L)$ of this line to be the real existing relation between L and M . The function $\omega = f(R)$ may be found from this equation, when not as an analytical expression, yet at least tabularly or graphically.

In order to reach some result in uncertain cases too, we must bear in mind that a relation between ω and R undoubtedly will appear from a correlation between L and M , whether linear or not. This correlation may be investigated in the way above indicated. If it turns out to be possible to find a function $U(L)$ of L and a function $V(M)$ of M , between which there is unimodular linear correlation — preferably with a large coefficient of correlation — then the most probable relation between L and M is expressed by $U(L) = V(L)$. From this equation the function $\omega = f(z)$ may be derived. In a similar way we may inquire whether the unequality between r and r' is a merely apparent one, in other words: whether the real equality is only disturbed by chance, or this unequality is in reality caused by a difference in the structure of the functions $r(x, x')$ and $r'(x, x')$. Here statistical considerations too must decide.

We can first examine whether there perhaps exists a functional relation between r and r' , different from $r = r'$. For that purpose we make use of the method of correlation — just as in the case of ω and R . As variables we introduce $l = \log r$ and $l' = \log r'$. Interpreting these quantities as coordinates of the point (l, l') three cases may occur:

- 1°. The points (l, l') lie within a rather narrow strip round the straight line $l = l'$; we may then conclude that r and r' are really equal.
- 2°. The points (l, l') lie rather close round another straight line, or round a curved one; the equation $l' = \Phi(l)$ of this line may then be considered as the real relation between l and l' . Then from $l' = \Phi(l)$ we may derive the relation between r and r' , be it only tabularly or graphically.

- 3°. The points (l, l') are spread so chaotically through the plane, that no dependence at all can be discovered between l and l' ; so we con-

clude, that there is no relation between r and r' , or, in other words, that the function $r(x, x')$ is independent of the function $r'(x, x')$.

Here, too, we obtain the most reliable relation between r and r' when we derive it from a correlation, linear or not, between l and l' . If we succeed in constructing a function $u(l)$ and a function $u'(l')$ between which unimodular linear correlation exists — if possible with a large coefficient of correlation — then the most probable relation between l and l' is represented by $u(l) = u'(l')$. From this equation we may finally derive the functional relation between r and r' .

If no traceable relation between r and r' can be found, we should try to determine r and r' as functions of x and x' (or of z and z'). As a rule, however, this difficult investigation will appear to be impracticable in consequence of the scantiness of the statistical data we have at our disposal.

In using the method of skew correlation in tracing the functional relation between ω and R (or between r and r') (this method in its turn resting on the knowledge of those functional relations) we should be inclined to suspect that we are reasoning in a vicious circle. Yet this fear is not justified, since a rather rough idea about the relation existing between ω and R (or r and r') suffices already to refine considerably the solution of the problem of skew correlation.

If a functional relation $\omega = f(R)$ is found, it may be utilised for adjustment. Of the four quantities $z_k, z'_k, \zeta_{kl}, \zeta'_{kl}$ the two latter are always much more uncertain than the former, and that ¹⁰ as in computing ζ_{kl} and ζ'_{kl} many neglects are committed, ²⁰ as they are derived from rather small frequency series (of R_k and R'_k individuals, see (21) and (21')). So the quantities ζ_{kl} and ζ'_{kl} first require adjustment.

This adjustment might be performed in the following way:

Replacing in (34) r by R and ω by $f(R)$, the equation thus modified:

$$\frac{z^2 - 2 \cos \{f(R)\} \cdot zz' + z'^2}{\sin^2 \{f(R)\}} = R^2$$

furnishes a value of R to each combination (z_k, z'_k) . Although the structure of this equation in R may be rather complicated, the fact that the solution usually differs little from the value $\sqrt{rr'}$ empirically given, will lead to simplifying the operations.

Thus, to z_k, z'_k the value of R being found, we obtain the corrected corresponding value of ω from $\omega = f(R)$, the equations $z^2 + \zeta^2 = R^2$, $z'^2 + \zeta'^2 = R^2$ furnishing the corrected values of ζ_{kl} and ζ'_{kl} .

In the most general case ($r' \neq r$) a relation between r and r' may be of service in adjusting.

r' being known as a function of r , we also know $\frac{r'}{r}$ as a function of rr' , thus (see (46) and (47)) λ^2 as a function of R^2 , or λ as a function of R .

From z_k, z'_l and the (provisionally accepted) empirical values of ζ_{kl}, ζ'_{kl} , we may compute r and r' (thus also $R = \sqrt{rr'}$) by means of (25), R giving in its turn a value of λ . Then the equation (48) furnishes z and z' , after which the equation (49) gives a value of ω . The equation (32) also furnishes ω , but the value of ω thus obtained is rather uncertain. We may consider the value of ω derived from (49) as correcting the value of (32). Finally, from (44) and (45) we find the corresponding values of ζ and ζ' .

The method of treating skew correlation sketched above may be illustrated by an example.

This example refers to a wood of djati trees, situated in the Dutch-Indies forestry Wanas, (Res. Rembang, Java), section Katessan, Park 102 (Remaining Stand and Thinning Stand).

The data have been collected by Mr. H. E. WOLFF VON WÜLFING, Forest-officer at the Forest Research Institute at Buitenzorg, who kindly put them at our disposal.

Mr. WOLFF VON WÜLFING has measured the trunk diameter, height, and volume of each tree.

In the frequency table treated here the correlation is investigated between the volume x (unit 1 dM³) and the height x' (unit 1 dM).

The table added to this records the observed frequencies Y_{kl} . In the outer column to the right the total frequency contents R_k of the rows ξ_k are noted. At the bottom the total frequency contents R'_l of the columns ξ'_l are recorded. The last compartment of the bottom bears the total number $\sum_{k=1}^n R_k = \sum_{l=1}^{n'} R'_l = N = 916$.

If we treat this frequency table according to the method of linear correlation, we find:

$$\bar{\xi} = 57,845, \bar{\varepsilon} = 47,37; \bar{\xi}' = 11,909, \bar{\varepsilon}' = 2,772; \gamma = 0,831.$$

Besides there is found (see p. 801 (p. 5)):

$$S = +0,978, S'_1 = +3,007, S_1 = +1,518, S' = +0,950;$$

$$E = -2,000, E'_1 = +6,803, E_2 = +2,082, E_1 = +0,154, E' = -2,205.$$

These results show that the data fulfil in a very unsatisfactory way the conditions of linear correlation, so that it is quite reasonable to apply the method of skew correlation.

From the frequency table the following values are successively calculated:

a. the values of z_k and z'_l (by (19), (8), (19') and (8')), the values of $\zeta_{k-1/2, l}$ and $\zeta'_{k, l-1/2}$ (by (21), (8), (21') and (8')), and — by (linear) interpolation — the values of ζ_{kl} and ζ'_{kl} ;

b. the values of $r^2 = z^2 + \zeta^2$ and $r'^2 = z'^2 + \zeta'^2$;

c. the values of $A = zz' - \zeta\zeta'$ and $B = z\zeta' + z'\zeta$;

d. the values of $M = \operatorname{tg} \omega = \frac{B}{A}$.

We very much regret that — owing to pressure on our space — we

are obliged to omit the tables recording the results of calculation mentioned sub a.—d.

However we attach a certain value to the addition of some graphs to the text, viz.:

1⁰. The graph of the combinations $l = \log r$ and $l' = \log r'$.

This diagram shows that we may safely go on assuming the equality of r' and r , $r' = r$.

2⁰. The graph of the combinations $L = \log R = \log \sqrt{rr'}$ and $M = \operatorname{tg} \omega$

This diagram does not suggest a conspicuous relation between ω and r ; so we are probably right in considering ω as a constant. For this angle we have found — by adjustment of $M = \operatorname{tg} \omega$ — : $\bar{\omega} = 18^\circ 38' 30'' \pm \pm 19' 15''$, whence

$$\bar{\gamma} = \cos \bar{\omega} = 0.948 \pm 0.002, \quad \sin \bar{\omega} = 0.320.$$

So this value of the coefficient of correlation is larger than that computed by the less appropriate method of linear correlation.

3⁰. The graph of the function $z(x)$, plotted in a natural scale.

The course of the function $z(x)$ suggests that it answers to an equation of the form ¹⁾

$$z = \lambda \cdot {}^{10}\log \frac{x - x_0}{x_m - x_0},$$

where λ is a constant, x_0 the lower limit of x , x_n the upper limit of x , x_m the median, i. e. the value of x which corresponds to $z = 0$.

4⁰. The graph of the equation last mentioned, plotted in a one-sided logarithmic scale viz.:

$$\begin{array}{ll} \dots & \text{with } x_0 = 0 \quad \left(z = \lambda \cdot {}^{10}\log \left(\frac{x}{x_m} \right) \right) \\ \circ \circ \circ \circ & \text{,, } x_0 = -30 \\ \times \times \times \times & \text{,, } x_0 = -75 \\ \square \square \square \square & \text{,, } x_0 = -225. \end{array}$$

Experiments with other values of x_0 have also been made; they have however — for clearness' sake — not been represented in the diagram.

The points $\times \times \times \times$ appeared to lie best in a straight line; for this line is found:

$$x_0 = -75 \text{ (dM}^3\text{)}, \quad x_m = 47 \text{ (dM}^3\text{)}, \quad \lambda = 4.30.$$

So the most reliable function $z(x)$ is:

$$z = 4.30 \cdot {}^{10}\log \left(\frac{x + 75}{47 + 75} \right),$$

whence

$$\frac{dz}{dx} = \frac{K}{x + 75}, \quad (K = 4.30 \times 0.4343 = 1.87),$$

so that we find for the reaction function

$$\eta = \frac{dx}{dz} = k(x + 75).$$

¹⁾ J. C. KAPTEYN and M. J. VAN UIVEN: Skew Frequency Curves in Biology and Statistics, 2nd paper, p. 46.

5°. The graph of the function $z'(x')$, plotted in a natural scale.

The course of the function $z'(x')$ suggests that it answers to an equation of the form¹⁾

$$z' = \lambda' \cdot {}^{10}\log \left(\frac{x' - x'_0}{x'_{n'} - x'} : \frac{x'_m - x'_0}{x'_{n'} - x'_m} \right),$$

where the quantities λ' , x'_0 , x'_m have a meaning analogous to that in the former case, $x'_{n'}$ representing the upper limit of x' .

6°. The graph of this last equation, plotted in a one-sided logarithmic scale viz.:

$$\begin{array}{ll} \dots & \text{with } x'_0 = 0, x'_{n'} = \infty \quad \left(z' = \lambda' \cdot {}^{10}\log \left(\frac{x'}{x'_m} \right) \right) \\ \square \square \square \square & \text{,, } x'_0 = 10, x'_{n'} = 200 \\ \times \times \times \times & \text{,, } x'_0 = 20, x'_{n'} = 180 \\ \circ \circ \circ \circ & \text{,, } x'_0 = 47, x'_{n'} = 173. \end{array}$$

Experiments with other values of x'_0 and $x'_{n'}$ have also been made, but have not been represented in the diagram.

The points $\circ \circ \circ \circ$ appeared to deviate least systematically from a straight line. For the line best adapted to these points we have found:

$$x'_0 = 47 \text{ (dM)}, x'_{n'} = 173 \text{ (dM)}, x'_m = 121 \text{ (dM)}, \lambda' = 1.44.$$

Thus the most reliable function $z'(x')$ is:

$$z' = 1.44 {}^{10}\log \left(\frac{x' - 47}{173 - x'} : \frac{121 - 47}{173 - 121} \right),$$

whence

$$\frac{dz'}{dx'} = K' \left(\frac{1}{x' - 47} + \frac{1}{173 - x'} \right) = \frac{126 K'}{-8131 + 220x' - x'^2}, (K' = 1.44 \times 0.4343 = 0.625)$$

so that we find for the reaction function

$$\eta' = \frac{dx'}{dz'} = k' (-8131 + 220x' - x'^2).$$

Finally, from the above results the unimodular final variables are found to be

$$t = \frac{z}{\sin \omega} = \frac{4.30}{0.320} \cdot {}^{10}\log \left(\frac{x + 75}{47 + 75} \right) = 13.44 \cdot {}^{10}\log (x + 75) - 28.04$$

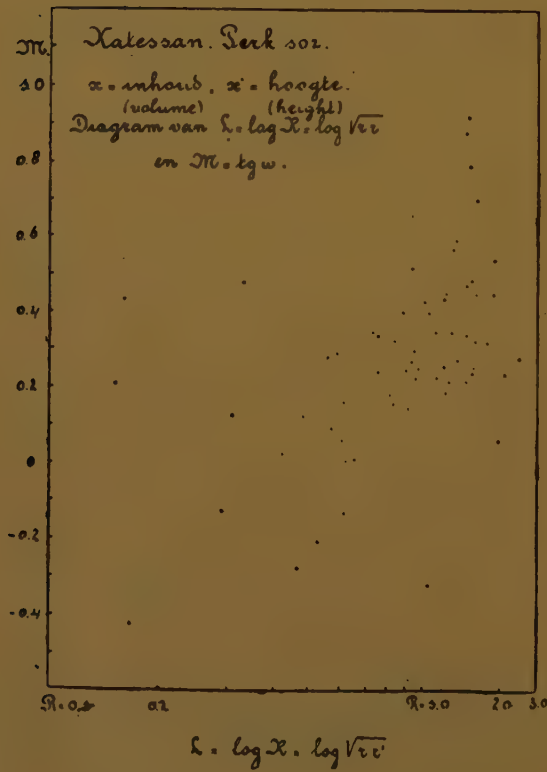
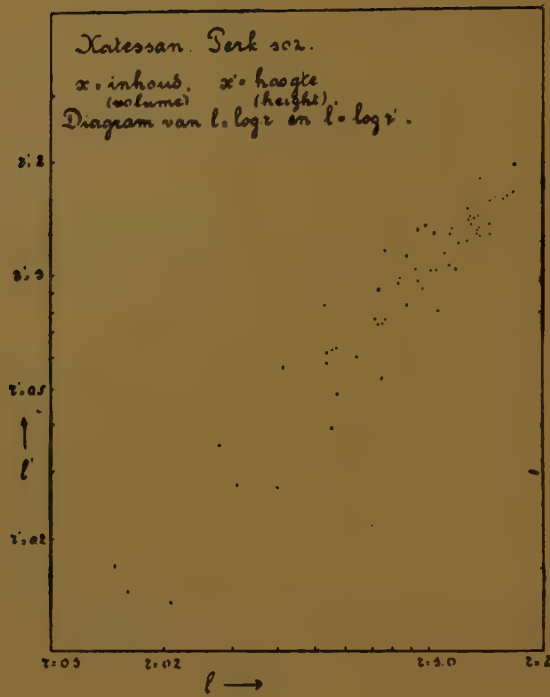
$$t' = \frac{z'}{\sin \omega} = \frac{1.44}{0.320} \cdot {}^{10}\log \left(\frac{x' - 47}{173 - x'} : \frac{121 - 47}{173 - 121} \right) = 4.50 {}^{10}\log \frac{x' - 47}{173 - x'} - 0.69$$

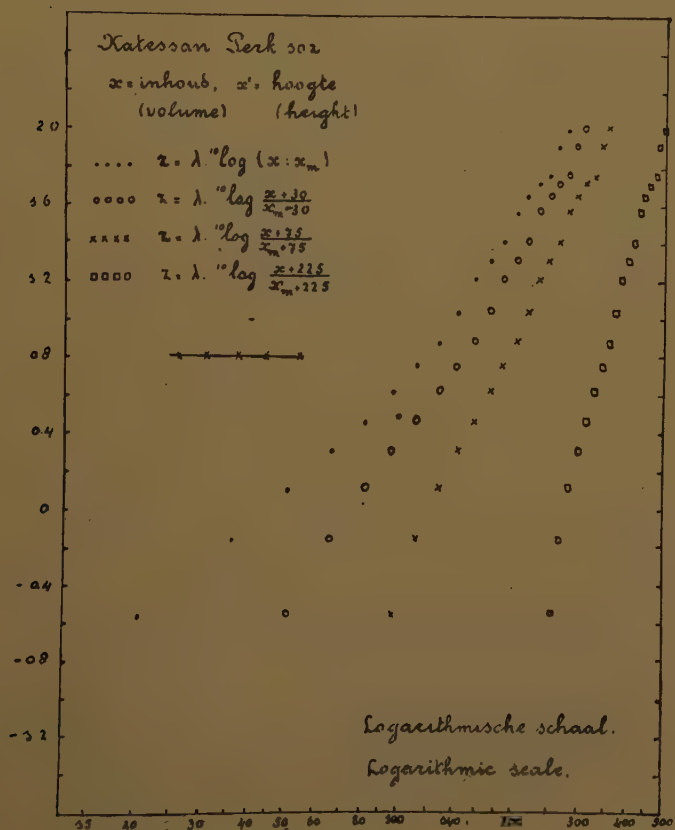
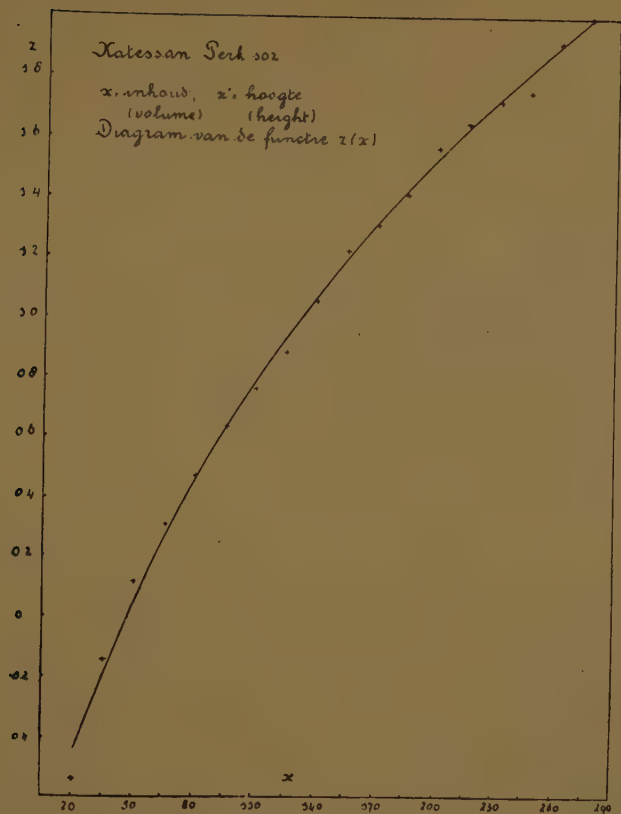
with $\gamma = 0.948$.

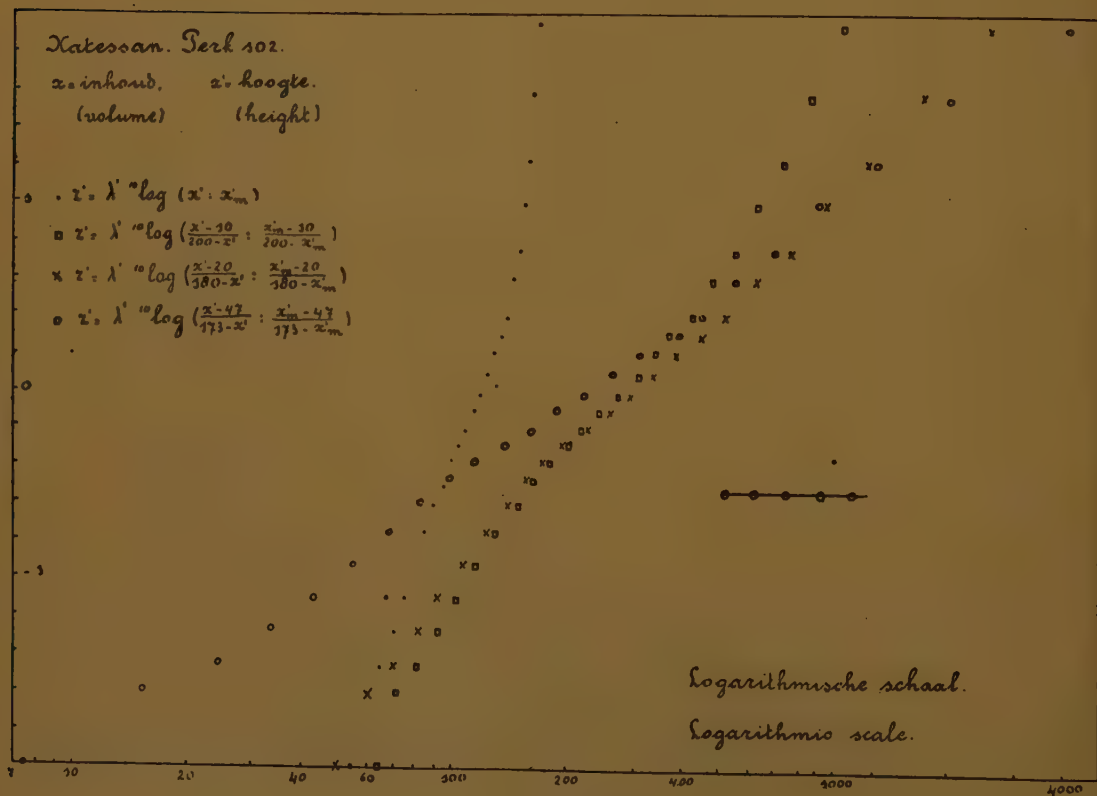
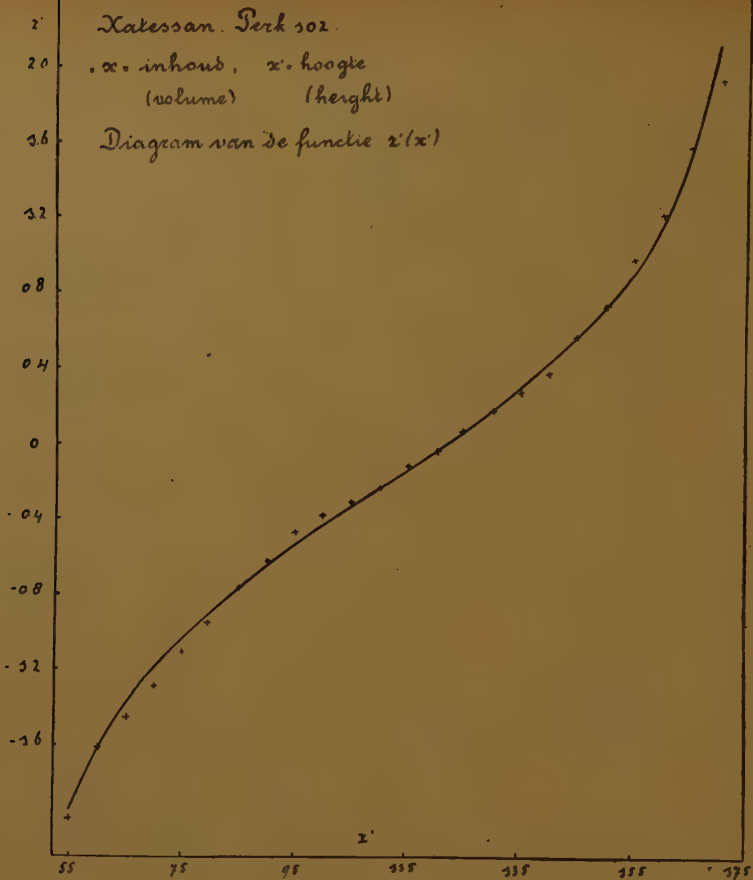
¹⁾ M. J. VAN UVEN. Logarithmic Frequency Distribution. These Proceedings 19, 1916, p. 533. This formula answers to a quadratic reaction function. Perhaps a more subtle analysis would add a cubic term to this function.

KATESSAN, PARK 102. ~ x = VOLUME, x' = HEIGHT. ~ TABLE OF THE OBSERVED FREQUENCIES.

$x' \backslash x$	52.5	57.2	62.5	67.5	72.5	77.5	82.5	87.5	92.5	97.5	102.5	107.5	112.5	117.5	122.5	127.5	132.5	137.5	142.5	147.5	152.5	157.5	162.5	167.5	172.5	
12.5	2	8	7				35	34	24	18	7		1													201
27.5				1			9	13	26	18	32	29	25	18	8	2	1									182
42.5								1	2	2	3	7	23	19	32	24	14	3	2		1					133
57.5												2	1	6	14	27	14	14	12	5	1					96
72.5															2	4	14	13	21	10	6	2				72
87.5																1	2	11	19	14	11	3	1			62
102.5																	1	1	12	12	9	4	2			41
117.5																		2	5	6	13	3	4			33
132.5																			4	3	10	9	6	1		33
147.5																			3	3	7	7	5			25
162.5																					3	4	1	1		9
177.5																			1		2	1	1	3		8
192.5																						4	4		1	9
207.5																							1	1	3	
222.5																						1	1		2	
237.5																					1				1	
252.5																							1	2	3	
267.5																									1	
282.5																							1	1	2	
	2	8	7	14	22	30	44	48	52	38	42	38	50	43	56	58	46	44	79	53	63	38	28	10	3	916







Endocrinology. — *“Further communications about Menformon, the hormone of the estrous cycle. (Reactivating influence upon senile mice, anti-masculine action, influence upon metabolism.)”* By ERNST LAQUEUR, P. C. HART and S. E. DE JONGH. (Communicated by Prof. R. MAGNUS.)

(Communicated at the meeting of February 27, 1926).

I. *Influence upon senile mice.*

In a previous communication¹⁾ we described how we determined the action of a water-soluble female sexual hormone we prepared and for which we chose the name Menformon. We made use of the fact that such a substance, as the important experiments of ALLEN and DOISY have shown, is able to cause in the vagina of castrated rats and mice characteristic changes identical with those occurring in the spontaneous estrus, and we wanted that by the so-called “unit” at least the stage analogous to the pro-estrus should be passed.

A few times we tried to investigate whether in senile non-castrated mice which do not show any more estrous phenomena, these occur anew after injection of Menformon. By previous observation of several months' duration we knew that they had shown more or less regular cyclic estrous changes, but that these changes had been missing during the last weeks. Of course the animals had been controlled every day by means of smears²⁾. To give an example: Mouse B₁, under observation since 199 days; during the first 157 days 15 estrous periods (9 obvious and 6 indefinite) occurred, during the next 41 days none: we then gave 3 times 0.3 ccm of Batch 120 aq, altogether about 5 M.U. with a dry residue of 0.03 mgr. Two days afterwards a strongly positive reaction was seen, then again after 17 days.

In a communication which appeared three months ago STEINACH³⁾ states to have obtained similar results in rats with the extracts he prepared. The amount of solids he injected, however, is several thousand times larger, i.e. about 225 mgr. STEINACH further reported a fact which up to this moment we have been able to confirm only once, i.e. that not only the estrus reappeared, but that a real rejuvenation took place, in that sense that the ovaries too took up their function again so that after the injection spontaneous cycli occurred. This of course is a very important observation.

¹⁾ These Proceedings 28, p. 890, 1925.

²⁾ A second control of these preparations was performed by Dr. WIJSENBECK.

³⁾ PFLÜGER's Arch. 210, 4/5, 588, 1925.

II. *Anti-masculine action.*

In our previous publication we said that after 8 to 9 injections of Menformon in young immature rats and guinea pigs the female genitals develop within 9 to 10 days, so that these are equal to the organs of older, more mature animals. We have been able to confirm this once more in another rat, the control animal having been injected with liver extract prepared in a similar way as Menformon is made from follicular liquid, from corresponding quantities of liver. It was shown that this last animal possessed much smaller genitals.

Another experiment on the contrary in which the animals had only received injections during five days and had been killed after another five days proved negative. Here the dimensions of the genitals did not differ from those of the controls. This leads to the conclusion that the injections must be continued for a certain period of time to produce an obvious difference in development between the animals.

Several authors (STEINACH, ATHIAS and MOORE¹), confirmed by LIPSCHÜTZ²) in a series of recent publications) claimed that ovaries or parts of these on implantation into a male animal can inhibit the development of specifically masculine organs and that simultaneously a certain development of female characteristics, a stronger development of the mamillae



Fig. 1. On the left side rats N°. 9 and 7 (control animals injected with liver extract) on the right side Rats N°. 10 and 12 (injected with Menformon).

¹) For literature see WIJSENBECK, Ned. Tijdschr. v. Geneesk. 1924, II, 2746.

²) PFLÜGER's Archiv. 211, part. 6. 1926, and previous volumes.

especially, occurs. We now tried to obtain a similar anti-masculine action with Menformon.

Of six young, three weeks old, male rats, which were left with their mother, three were injected with Menformon, the other three with the liver extract prepared in the same way: the injections were started on Dec. 16th. The Menformon-animals got 3 M.U. every day, the others a similar quantity of the liver-extract. As one of the Menformon-animals died on January 29th, a control animal was killed on the same day; a second pair was killed on February 1st, the last pair on February 10th. Because we did not use the purest preparations every Menformon-animal got in 55 injections altogether 165 M.U. with a content of solids of 10.6 mgr, whereas every control animal got 20.2 mgr. of the liver extract. The accompanying figure 1 shows very clearly the difference in dimensions of the genitals of two of the three pairs (on the left side the control rats Nrs. 9 and 7, on the right side the Menformon-animals Nrs. 10 and 12).

Fig. 2 shows the microscopic appearance of cross sections of the seminiferous tubules, on the left from control-rat Nr. 7, on the right from Menformon-rat Nr. 12.

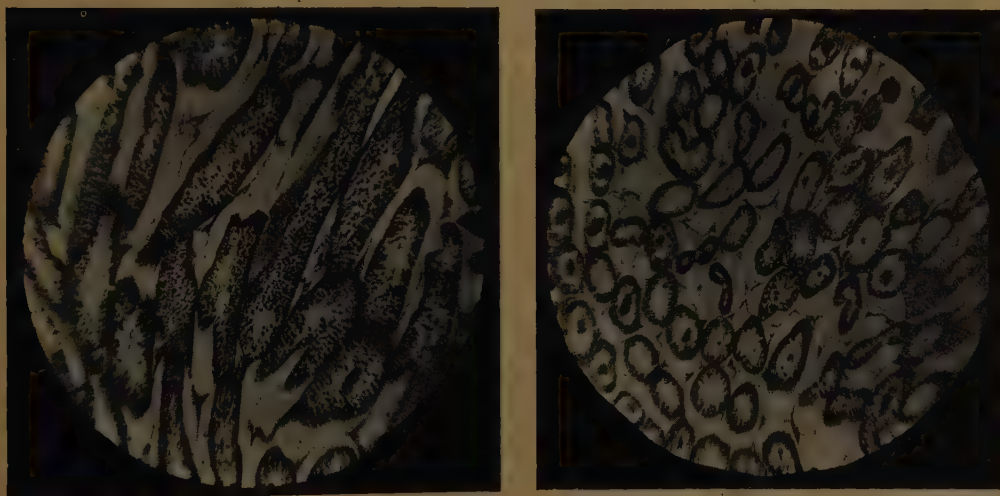


Fig. 2. Seminiferous tubules, on the left from control-rat N^o. 7, on the right from Menformon-rat N^o. 12.

The animal treated with Menformon only shows a thin epithelial covering of the walls, whereas in the control animal the tubules are partly filled with cells showing a beginning spermatogenesis. The results of this experiment are summarized in Table I.

From this table results that in all Menformon-animals the total weight after the experiment was somewhat less than in the control rats, but that the weight of the genitals was much more in arrear. The difference amounts here to 120 per cent, whereas the difference in body-weight is

TABLE I.

(The table does not only give the weight of the testes, but also that of the thymus and the adrenals).

	Number of animal	Weight (grs.)		Genitals (mgr.)	Thymus (mgr.)	Adrenals (mgr.)	
		before	after				
Control animals (Liver)							
29/1	9	15	40	336.6	68.0	13.4	
1/2	7	17	44	345.1	111.7	16.7	
10/2	8	16	66	680.2	205.4	18.4	
Average		16	50	487.3	128.4	16.2	
Menformon animals							
29/1	10	15	30	124.4	13.4 (l)	21.4	
1/2	12	15	42	200.4	93.0	18.6	
10/2	13	15	51	336.8	140.8	20.6	
Average		15	41	220.5	82.4	20.2	
Percentile difference = $\frac{\text{Control animals}}{\text{Menformon animals}} \times 100$							
		7	22	121	56	—20	

only 22 per cent. Besides attention is drawn by the fact that the thymus in the Menformon animals is smaller, whereas the adrenals are somewhat larger.

As these differences of adrenals and thymus occurred in all three pairs of animals they are probably not caused by chance.

To explain the fact that the thymi are smaller one might think of the overflowing of the body with sexual substances of which we know that during puberty they assist in causing the thymus atrophy. Then the thymus would have no sex-specificity, because it reacts in this case upon a surplus of the hormone of the opposite sex.

Regarding the adrenals some authors claim that the cortex especially has something to do with female sexual life and increases in size at its heights. So there is no reason to be astonished at the adrenals of male animals treated with female hormone being larger than those of the controls.

As the body weight of animals which are not necessarily in the same state of nutrition is an incorrect criterion to compare to the weight of the organs, we determined for the set of rats Nrs 8 and 13 the weight of some organs whose dimensions in all probability are not influenced by Menformon. The

liver, and especially the heart, kidneys, and spleen differed less in weight than the total animals.

This accentuates the differences of genitals and thymus. (See Table II.)

TABLE II.

Animal	Weight in grams	Heart in mgr.	Spleen in mgr.	Kidneys in mgr.	Genitals in mgr.	Thymus in mgr.	Adre- nals in mgr.	Liver in mgr.
8	66	378	439	956	680	205	18	4360
13	51	321	413	895	337	141	21	3431
Difference per cent	29	17	6	13	202	46	-10	27

The weights were determined within tenths of milligrams, but were rounded off in the table.

III. *Influence on metabolism.*

Something concerning the influence of Menformon upon metabolism in castrated female rats has been mentioned in our German publication¹⁾.

The experiments which have meanwhile been extended are briefly related below.

The influence of ovarian substances upon metabolism has already been investigated repeatedly. We only mention here the researches of DE VEER in the laboratory of KOCHMANN in Halle, who used rats for his experiments, and those of ZONDEK in the "University Women Hospital" of FRANZ at Berlin, who administered Ovarnon and Ovowop respectively to female patients. These as well as all previous similar experiments have been carried out with substances containing an exceptionally large amount of impurities, so that it is very difficult to see clearly an eventual specific influence.

We only injected 1 cubic centimetre of water with 0.05 to 0.90 mgr of solids.

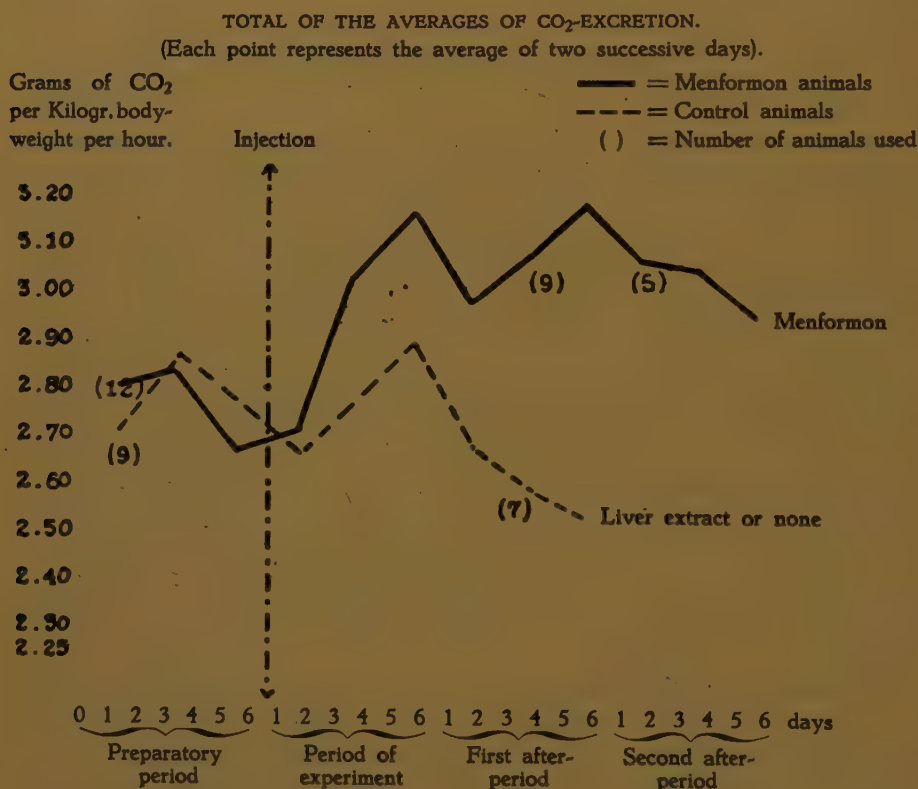
The method used was that of DANOFF (from ASHER's laboratory) with a few changes we thought useful.

The apparatus was constructed in such a way as to enable us to include several (up to 6) animals in one experiment. This was done because we thought it necessary to work with several animals at a time, as work in other fields of internal secretion had shown us the necessity of doing this, especially to exclude the so-called "Day-factors". The determinations were made every day during three or four weeks, with the exception of a single Sunday in the beginning or towards the end of the experiment.

¹⁾ Deutsche Mediz. Wochenschr. Numbers 1 and 2, 1926.

Every determination lasted three hours. The rats fasted for at least 15 hours before the experiment, whereas they had been accustomed before to eating in the remaining 6 hours so much that their body weight remained practically constant. We determined (on a gold balance) with an accuracy within 10 milligrams: the weight of the rats before and after the experiment, that of the tubes with sulfuric acid and with calcium chloride and of those with sodium-lime, whose increase in weight showed the amount of water and carbon dioxide excreted. From the difference between the loss in weight of the animals and the increase in weight of all the tubes together the oxygen-intake was calculated.

In a first series of experiments determinations were made upon six rats which were always used simultaneously and of which one died before the end of the experiment. All animals got on the same day about 5 M.U. of Menformon (Batch Ov. 17) in three injections of 0.4 ccm each, altogether 0.9 mgr of solids.



The second series of experiments included three rats which received in all 1 ccm = 16 M.U. (Batch 117 aq, altogether < 0.05 mgr), and two animals which were injected with liver extract in corresponding quantities (about 1 mgr of solid matter). The third series was formed by 4 Menformon animals (Batch 120 aq, 1 ccm = 5 M.U. = 0.4 mgr of

solids), 4 liver-animals (each 1.2 mgr of solids) and moreover 3 animals which were not injected at all. In the second and third series the Menformon rats showed a definite estrus, whereas metabolism was increased in all three series of these animals.

Instead of giving many hundreds of figures separately we resume the results in a curve showing the average CO_2 -excretion of all animals used. As the Respiratory Quotient remains almost unchanged the O_2 -curve runs parallel with the above. To exclude daily variations which are of no interest for the endresult and which would interfere with its clearness, each point in the curve represents the average of two successive days.

The fact that the Menformon-curve remains high during so long a time is explained by the fact that the protracted action occurred just in that series in which no control animals were used.

Conclusions.

I. In some senile female mice in which spontaneous estrous phenomena had been lacking since many weeks we succeeded in causing an artificial estrus by three injections of Menformon given within one day.

II. In connection with previous experiments in which Menformon had shown a growth-promoting action on the female organs of generation, an antimasculine influence of this hormone was found in three rats in which the growth of the male genitals was inhibited as compared with three brothers from the same litter that were injected with liver extract. Moreover in these animals the thymus had diminished, the adrenals increased in size.

III. In three series of experiments on castrated female rats, each including from 5 to 11 animals, a definite increase in gaseous metabolism was found after injection of Menformon, whereas similarly castrated control animals that got nothing or only a liver extract and were used on the same days, showed nothing or only a much smaller increase.

*Pharmacotherapeutic Laboratory of the University.
Amsterdam, February 1926.*

Chemistry. — "*On the Action of Dibenzoylperoxide on Benzene at Low Temperatures in the Presence of Anhydrous Metal Chlorides.*" (Contribution to the knowledge of catalytic phenomena.) By Prof. J. BÖESEKEN and A. F. A. REYNHART.

(Communicated at the meeting of November 28, 1925).

Introduction. The action of benzoylperoxide on a great number of substances has been subjected to a thorough examination by H. GELISSEN ¹⁾, partly in collaboration with P. H. HERMANS ²⁾. In this investigation a number of remarkable conversions were found, the observations of earlier investigators were improved upon, and could be explained for the greater part.

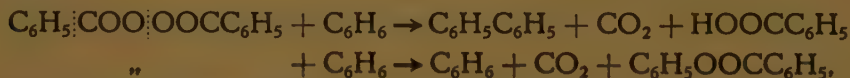
Chiefly the action on boiling CCl₄ ³⁾ and benzene (loc. cit. p. 285), which takes place at about 80°, has thrown light on the subject.

In the first reaction more than one molecule of carbonic acid gas is developed, *ω*-trichlortoluic acid (Cl₃C₆H₄COOH) being formed as chief product. It was natural to assume that tetrachlorine was distributed over the benzoylperoxide as follows :

$$\text{C}_6\text{H}_5\text{:COO:OCC}_6\text{H}_5 + \text{CCl}_4 \rightarrow \text{C}_6\text{H}_5\text{Cl} + \text{CO}_2 + \text{CCl}_3\text{C}_6\text{H}_4\text{COOH};$$

this was, however, proved only by the action of boiling benzene ⁴⁾.

Then were formed : CO₂, diphenyl, benzoic acid, terphenyl, quaterphenyl, phenylbenzoate and considerable quantities of resin. The quantities of benzoic acid were very considerable, hence a simple decomposition into diphenyl + 2 CO₂ did not take place. Besides the quantity of reaction product was greater than the quantity of peroxide, which was started from. The benzene must, therefore, have come in reaction, and this in two directions :



which is further proved by not boiling benzoylperoxide with benzene, but m.m.dinitrobenzoylperoxide and p.p. dichlorbenzoylperoxide, in which mono-m-nitro- resp. p.chlordiphenyl was obtained instead of di-substituted diphenyl.

In this way Mr. GELISSEN has proved that at about 80° a pretty smooth reaction takes place, in which the solvent participates. He showed that

¹⁾ Thesis for the doctorate by Ir. H. GELISSEN, Delft 1925.

²⁾ Berichte **58**, 285, 476, 479, 764, 765, 770, 984, 2396. (1925).

³⁾ Recueil **43**, 869 (1924).

⁴⁾ GELISSEN and HERMANS, Ber. **58**, 286 (1925).

only one molecule of CO_2 was developed and that the solvent combined with the unequal rests of C_6H_5 and $\text{OOC}\text{C}_6\text{H}_5$ of the peroxide-molecule according to the R-H-schema. The benzene splits up into C_6H_5^- and H , the tetrachlor carbon into CCl_3 and Cl , etc.

Also the hydrolysis reaction, which was studied by v. BAEYER, and in which no CO_2 was split off, could be explained by means of the same schema :

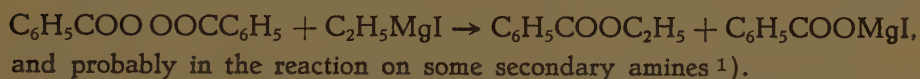


though a splitting up of the oxygen bridge is possible here.

This splitting up sets certainly in in the action of NaI in acetic solution :



It has likewise been established in the case of the reagent of GRIGNARD :

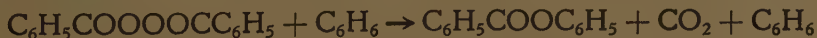


These two latter reactions take place at ordinary temperature ; hence it is not excluded that the asymmetric decomposition appears especially when the molecule, e.g. through increase of the temperature, starts splitting off carbonic acid. The decomposition will then begin with the formation of one molecule of CO_2 ; if the solvent is more or less active, the decomposition takes place in main lines according to GELISSEN's R-H-schema.

If one succeeds in making the reactions, which at first set in at this critical point, i.e. at the beginning of the self-decomposition of the peroxide, take place at much lower temperature, the course may be entirely different, because now the reaction is no longer forced in a definite direction by the self-decomposition of the peroxide.

We have succeeded in making the benzene act on the peroxide at much lower temperature by making use of catalyzers, as AlCl_3 , FeCl_3 , and SbCl_5 , and have found that the reaction actually proceeds in an entirely different direction.

The two first catalyzers had already been used by GELISSEN and HERMANS ²⁾, but because the investigation was made under the same circumstances as without catalyzer, i.e. at the boiling-point of benzene, these investigators assumed that the reaction took place according to the H-R-schema. In presence of the catalyzer the secondary reaction :



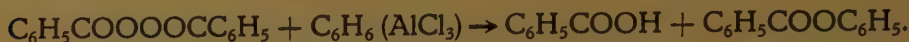
would have been favoured compared with the principal reaction (diphenyl + CO_2 + benzoic acid), because much more phenylbenzoate had been formed than would have been the case without catalyzer.

¹⁾ GAMBARJAN. Ber. 58, p. 1775 (1925).

²⁾ Ber. 58, p. 479 (1925). Compare Thesis p. 77—80.

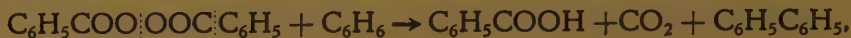
AlCl₃ as catalyzer.

If to a solution of 1 mol. of benzoylperoxide in excess of benzene one molecule of AlCl₃ is added, a reaction takes place already at 0°. Hardly any CO₂ is developed (only 0.02 mol.), and almost quantitatively one mol. of benzoic acid and 1 mol. of phenylbenzoate have been formed :



Hence GELISSEN and HERMANS' view cannot be maintained.

If the splitting off of CO₂ is prevented, the oxygen bridge is broken. For this reaction one molecule of AlCl₃ is necessary ; this combines with phenylbenzoate (an addition compound, already found by G. PERRIER¹), and is paralyzed by this. If it is taken into account that without catalyzer chiefly diphenyl, benzoic acid, and carbonic acid are formed :



it is seen that the catalyzer activates the bond between the oxygen atoms of the bridge, and this is broken already at low temperature.

Without catalyzer this place is inaccessible to the benzene ; only at higher temperature both this and the C₆H₅-bond become active, and the reaction sets in according to the asymmetric R-H-schema (GELISSEN and HERMANS loc. cit.).

The activation of the -O-O-bond by AlCl₃ draws again attention to the fact that the formation of a compound of the catalyzer with the molecules to be activated cannot account for the catalytic phenomena. For very probably the AlCl₃ attaches itself to the C=O-group (it forms very firm compounds with ketones), while another part of the molecule gets into reaction.

FeCl₃ as catalyzer.

At first we expected that this catalyzer would behave in the same way as AlCl₃, and we took 1 mol. of FeCl₃ to 1 mol. of peroxide. The reaction took place below 0° with slight generation of CO₂. After 24 hours the peroxide had disappeared ; no phenyl-benzoate could, however, be detected, and by the side of much more than one molecule of benzoic acid there had been formed a complex iron compound, in which there was a pretty large quantity of iron. As this reaction is a special example of catalysis, we shall return to it in a subsequent communication ; here we will only remark, that here too, as with AlCl₃, the primary reaction is a splitting up into one molecule of benzoic acid and one molecule of phenyl benzoate ; in the presence of benzene the phenylbenzoate is then further attacked by the catalyzer, in which by the side of benzoic acid dark-coloured compounds containing iron are formed.

As was remarked above this reaction proceeds very slowly below 8° and the generation of CO₂ is insignificant ; at the ordinary temperature this

¹) Bull. [3] 9, 1049 (1893).

becomes more important; also *diphenyl* is then formed. As appears from the subjoined table the quantities of CO_2 and diphenyl are equivalent; hence it is very probable that the reaction found by GELISSEN and HERMANS sets in by the side of the $-\text{O}-\text{O}-$ decomposition:

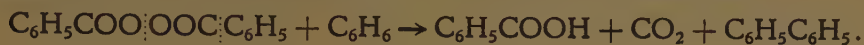


TABLE I.

The action of equimolecular quantities of peroxide and FeCl_3 on an excess of benzene.

t	Peroxide	FeCl_3	CO_2	$\text{C}_6\text{H}_5\text{OOOH}$	Phenyl benzoate	Diphenyl	Fe complex	Fe % in compl.
+ 35°	24 gr. (0.1 m.)	16 gr. (0.1 m.)	2.21 gr. (0.05 m.)	18 gr. (0.15 m.)	—	7.5 gr. (0.05 m.)	4 gr.	4.6 %
+ 6°	"	"	1.33 gr. (0.03 m.)	15 gr. (0.12 m.)	—	4.5 gr. (0.04 m.)	7 gr.	5.8 %
— 14°	"	"	0.92 gr. (0.02 m.)	14 gr. (0.11 m.)	—	2.75 gr. (0.018 m.)	8 gr.	6.2 %
— 30°	"	"	0.79 gr. (0.018 m.)	13.5 gr. (0.11 m.)	traces	2.5 gr. (0.016 m.)	10 gr.	7.0 %

TABLE II.

The action of benzene on peroxide in the presence of a small quantity of catalyzer.

t	Peroxide	FeCl_3	CO_2	$\text{C}_6\text{H}_5\text{COOH}$	Phenyl benzoate	Diphenyl	Fe complex
40°	12 gr.	0.8 gr. (0.005 m.)	0.213 gr. (0.005 m.)	7 gr. (0.058 m.)	1 gr. (0.005 m.)	0.75 gr. (0.005 m.)	2 gr. (4.5 % Fe)
20°	(0.05 m.)	"	0.150 gr. (0.004 m.)	5.5 gr. (0.045 m.)	2 gr. (0.01 m.)	0.400 gr. (0.003 m.)	3 gr. (5.1 % Fe)
0	"	1.6 gr. (0.01 m.)	0.725 gr. (0.016 m.)	9 gr. (0.074 m.)	2.5 gr. (0.013 m.)	2.77 gr. (0.018 m.)	6 gr.

On use of AlCl_3 one mol. per mol. of peroxide is required to cause the reaction to proceed to its end; but this is not the case with FeCl_3 . If e.g. 0.1 mol. per mol. of peroxide is used, the reaction reaches its end all the same after 24 hours. It is, however, self-evident that then this catalytic reaction proceeds more slowly than that with 1 mol. of FeCl_3 .

These observations are combined in table II. It appears that comparatively much diphenyl and CO_2 are formed also at low temperature, and that then the usual reaction according to the R-H-schema becomes of more importance.

Without AlCl_3 or FeCl_3 the splitting takes place at the phenyl nucleus and consequently also at the oxygenbridge; *with* these catalyzers the splitting takes place exclusively at the oxygenbridge.

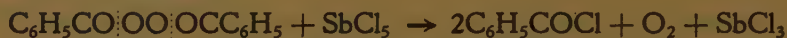
The two reactions can proceed side by side.

$ZnCl_2$ does not work accelerating, at 0° the peroxide has remained unchanged after 24 hours, save for a slight generation of CO_2 .

$SnCl_4$ is a very bad catalyzer. After 24 hours 0.8 gr. of benzoic acid had developed out of 12 grammes of peroxide and excess of benzene, also phenylbenzoate could be shown; practically no development of carbonic acid took place.

On action of $SbCl_5$ on a solution of peroxide and benzene a violent reaction took already place at 0° . If the temperature is kept low, a regular generation of gas takes place. This is carbonic acid only for a very small part, 0.015 mol., for the greater part it is hydrochloric acid; besides, we ascertained the formation of *oxygen* and of *benzophenon* in one experiment. On further examination it appeared that $SbCl_5$ acted on benzene already below 0° with formation of $SbCl_3$, HCl and dichlorbenzene, so that the reaction has a very complicated course here.

The formation of benzophenon indicates that an activation can take place of the $C=O \cdots O$ -bond:



which will have to be decided by a further study.

It is further our intention to examine a number of analogous chlorides and besides to replace the benzene by other hydro-carbons.

Delft, November 1925.

Anatomy. — "*On the Development of the Form of the Vertebral Spines in Mammals, especially in Man.*" By W. A. MIJSBERG. (Communicated by Prof. L. BOLK.)

(Communicated at the meeting of December 19, 1925).

The form of the vertebral spines differs largely in the different regions of the spinal column of man. It is especially the processus spinosi of the 2^d, up to and including the 6th cervical vertebra that differ from the others in possessing a bifid spine. In the so called lower races this terminal bifurcation is less pronounced and also less frequent than in the European. In other mammals it is entirely absent; only in apes, especially in anthropoids, do the spinous processes of some cervical vertebrae sometimes bifurcate. The records in the literature vary largely on this point; from them and from his own investigation LE DOUBLE¹⁾ concluded that only the epistropheus in the Chimpanzee possesses as a rule a bifid spine.

So with regard to the form of the processus spinosi of the cervical vertebrae man differs considerably from the other mammals. It is intelligible, therefore, that the question has often been considered what may be the cause of this deviating structure in man. According to the hypothesis, which has well-nigh become a dogma, that man has descended from more ape-like ancestors, this question has ever been formulated as follows: How did, in the phylogeny of Man, the bifurcated spinous processes in recent man originate from the unsplit cervical spines of his ancestors.

In his Memoir on the influence of the assumption of the erect attitude on the human frame RUGE²⁾ has expressed the opinion that also the characteristic form of the cervical spines in man is due to his erect stature. RUGE writes: (l.c. p. 10): "Auch die am Schädel festgeheftete Muskulatur beeinflusst am Rumpfe ihre Ausgangspunkte. Als augenfällige Zeichen hierfür sind die gespaltenen Dornen des 2. bis 6. Halswirbels zu nennen. Sie dienen unter anderem den selbständigen Muskeln des Nackens beiderseitig zum Ursprung und haben sich zugleich mit ihnen ausgebildet." VON EGGELING³⁾ has endeavoured to furnish further evidence for RUGE's hypothesis. He examined the cervical muscles of many monkeys and prosimiae, studied the form of the spinous processes of the cervical vertebrae of the animals he dissected, and subsequently tried, by comparison with

1) DOUBLE, A. F. LE, *Traité des variations de la colonne vertébrale de l'homme*. Paris. 1912.

2) RUGE, G., *Die Körperformen des Menschen in ihrer gegenseitigen Abhängigkeit und ihrem Bedingtsein durch den aufrechten Gang*. Leipzig. 1918.

3) EGGELING, H. VON, *Die Gabelung der Halswirbeldornen und ihre Ursachen*. Anat. Anz. Bd. 55. 1922. Idem, *Die Halswirbeldornen und deren Muskeln bei Halbaffen*. Ibidem.

the conditions in man, to ascertain whether there is any relation between the form of the spinous processes and the development of the muscles that take origin from them or are inserted in them. Three muscles are attached to the spinous processes: the *musculi spinales*, *interspinales* and *semispinalis cervicis*. The first-named muscle is so variable even in man that we need not take account of it. The *musculi interspinales* and the *m. semispinalis*, however, are muscles that are well-developed in man only in the cervical portion of the vertebral column, and consequently are characteristic of this region. They are much less pronounced in monkeys, where they are even vaguely differentiated from the musculature composing the deep muscles of the back. It will be seen then that the strong development in man of the muscles just mentioned, concurs with the terminal bifurcation of his cervical spines. VON EGGELING considers the strong development of the muscles in man to be owing to his having assumed the erect attitude, the muscles now having to sustain the head and to perform the movements of the head and the neck which had become more mobile in consequence of the erect attitude. These muscles having become stronger during the phylogeny of man should by their traction have caused the formation of the paired processes at the end of the cervical spines.

In this paper I shall abstain from criticizing VON EGGELING's work, referring for my critique and for details of my own investigation to my extensive treatise that will appear in the "*Zeitschr. für Anatomie und Entwicklungsgeschichte*". Nevertheless I wish to raise an objection to two essential points in the exposition given by RUGE and VON EGGELING.

First of all, in studying any problem in human phylogeny it is not right to start from the hypothesis that man descends from more ape-like ancestors. Facts carefully studied and discussed by BOLK, who based on them his fetalisation-theory, induce me to believe, as I have set forth in several papers, that in many respects the ancestors of man cannot be imagined more ape-like than recent man. In my opinion, therefore, for every problem concerning the descent of man we should try to find a solution by studying the available facts without vitiating our results by any preconceived idea.

My second objection to the exposition of RUGE and VON EGGELING is that they have endeavoured to establish the cause of the special form of the cervical spines in man, without ascertaining beforehand how the bifurcated spinous processes have sprung from the nonbifurcated processes. We gather from their reasoning that they consider it self-evident that the paired terminal processes are new osseous formations, new projections which they suppose to have been developed under the influence of muscular traction. They omitted to afford any evidence for this assertion. In order to obtain a better insight into the cause of the terminal bifurcation in man it was necessary to make a preliminary inquiry into the ontogenetic mode of development of the bifid spines of the cervical vertebrae in man, as well as of the unsplit *processus spinosi* in the other regions of the spinal column in man and in other mammals.

In the following pages I shall give a brief account of the results of this investigation beginning with a diagram of the modes of development of the cartilaginous processus spinosi.

Each vertebra develops from four cartilaginous centres. Two of them arise in the vertebral body and one in the basal part of each of the neural processes. The two cartilaginous centres in the vertebral body are soon fused. The cartilaginous processus neurales develop dorsad, and gradually enclose the spinal cord as semi-arches. Ultimately they unite dorsally to the spinal cord. The development of the processus spinosus may take place in various ways: we distinguish six types of development, as represented schematically in fig. 1.

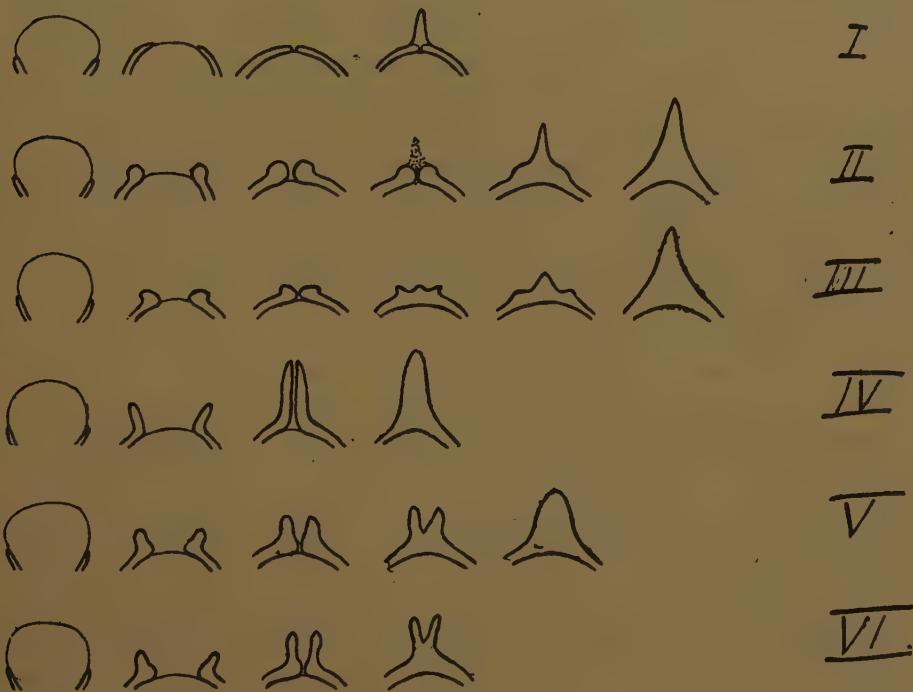


Fig. 1

Diagram of the different modes of development of the cartilaginous spinous processes in mammals.

1. In the first type the non-thickened ends of the semi-arches come in contact with each other. At the junction an unpaired outgrowth develops representing the anlage of the spinous process. This mode of growth occurs among Marsupials (*Dasyurus*, *Didelphys*).

2. While the vertebral canal is still wide open there appear at the semi-arches latero-dorsally directed terminal buds. When the spinal cord has been completely enclosed by the semi-arches, the thickened ends of the semi-arches meet in the dorsal median line. Then an unpaired median cartilaginous mass develops dorsally on the point of junction. In the typical

cases the growth of this median cartilaginous process is preceded by the formation of an unpaired, median precartilaginous outgrowth. A small part of the base of the cartilaginous processus spinosus is thus formed by the paired terminal protuberances of the semi-arches. In the beginning these buds can be recognized by a slight bulging, later on they are completely assimilated with the median process. This mode of development of the cartilaginous spines is very common among mammals. Typical cases, in which initially a precartilaginous median spine develops between and on the thickened ends of the semi-arches, I encountered in the thoracic vertebrae of man and the superior thoracic vertebrae of *Tarsius*. I detected a fine intermediate form at the 8th thoracic vertebra in a fetus of *Sciurus vulgaris*, 30 mm. in length. In this intermediate form there occur two cartilaginous terminal protuberances on the semi-arches, between and on which protuberances an unpaired mesenchymatous spinal anlage is found.

3. This developmental type differs from the preceding in that the terminal protuberances of the semi-arches are directed more laterad, and in that the median rudiment of the process is not very strong at first, so that a transient dorsal eminence is originated that is provided with three apices. Afterwards the median point gets more developed, in fact it constitutes nearly the whole process; the end-knobs of the semi-arches are merged into the base. This mode of development I could observe at the inferior dorsal vertebrae of *Tarsius*.

4. In this type the end knobs of the semi-arches are markedly prolonged. When the semi-arches come together dorsally to the spinal cord, their projections also adjoin, thus forming the paired rudiment of the whole spinous process; afterwards the halves coalesce over the whole length. This mode of development I observed very beautifully in the superior thoracic vertebrae of the sheep; probably it also occurs at some vertebrae of some other mammals (*Talpa*, *Sciurus*).

5. Just as in the preceding type long processes appear at the ends of the semi-arches, representing the paired rudiment of the spinous processes. The coalescence of the two halves takes place only in the basal part at first, so that for a time there exists a projection that is split at the end. Only after some time does the fusion become complete. The processus spinosus of the epistropheus of the rabbit, the rat, and the squirrel develops in this way; it would seem to me that probably the split process I found at the epistropheus of a *Didelphys auritus* (20 mm. crown—rump length) also belongs to this group.

6. Here the growth occurs initially in the same way as in the preceding type. The difference, however, is that the two processes, each of which represents the anlage of half a spine, only coalesce in their basal parts not transiently, as in the former type, but permanently.

The order in which the 6 developmental types have been described is not arbitrary: on the contrary they have been arranged so as to present progression in the intensity of two developmental changes. Generally

speaking we can say that a spinous processus is built up of an unpaired median rudiment growing out from the cartilaginous mass formed by the coalescence of the semi-arches, and a paired lateral rudiment: the protuberances or projections at the extremities of the semi-arches. In the first developmental type the spine develops from a median rudiment only, in the second a small paired rudiment shows itself which, as soon as the semi-arches come into contact, is overlapped by the median rudiment. With the third mode of growth the lateral rudiment persists a little longer, so that during a certain interval of time there exists a stage with three knobs. In the fourth type the lateral rudiment predominates: the median cartilaginous mass serves only to unite the semi-spines formed from the paired rudiment, but does not develop into an independent median rudiment of a process. In the fifth and the sixth type the median cartilaginous mass does not extend transiently, resp. permanently as far as the end of the semi-spines that have sprung from the lateral rudiment.

The extension of the median cartilaginous mass and its significance as median rudiment of the spinous processes decreases from the first to the sixth developmental type, whereas the significance of the paired, lateral rudiment rises.

Now the question arises, which of these developmental types is phylogenetically the most primitive. In order to find a plausible answer to this question I examined the way in which the spinous processes in lower vertebrates develop. Some Amphibians examined appeared to possess only a median unpaired rudiment; the paired lateral rudiment is lacking. Among the Reptiles I detected only in a few cases a slight, paired, lateral rudiment, arising only very late in the ontogeny and contributing little to the formation of the spinous process. It is presumable, therefore, that the developmental type sub 1 is to be considered also for the mammals as the most primitive mode of development of the spinous processes. During the phylogeny of different mammals changes have occurred, consisting in the progression of the paired lateral rudiment and a regression of the median rudiment. In this respect the various mammalia have deviated to a greater or lesser extent from the primitive mode of development: differences are even noticeable at the different regions of the spinal column of one and the same animal. The developmental type sub 6 may be considered as the most progressive (= non-primitive) type.

It appears then that in the phylogeny of mammals, in which spinous processes develop in one of the modes described sub 4, 5 or 6, a regression of the median rudiment has taken place. In contradiction to the principle laid down in the biogenetic law this regression is not repeated in the ontogenetic development; the new condition is brought about because the median rudiment no longer develops as completely as is the case with the primitive mode of development. We see, then, that phylogenetic regression takes place because an ontogenetic developmental process is arrested before it has reached completion. In this connection it is remarkable that with

a less intense departure from the primitive mode of development we do not yet find an arrest but only a retardation of the ontogenetic process of growth; thus with the 3rd developmental type the median rudiment no more prevails directly over the paired lateral rudiment; thus in the 5th type only transitorily a spine is formed, which is split at the end. It is clear especially in the transition from the 5th to the 6th type that the changes in the ontogenetic development which bring about the phylogenetic regression correspond to the principle expressed in BOLK's Fetalization.

On the whole a certain relation is to be noted between the part played by the lateral, paired rudiment and the median non-paired rudiment in the formation of the spinous processes: when the median rudiment gets strongly developed the paired rudiment is of little importance and conversely. Therefore, if we wish to solve the problem: what etiological factor is answerable for the appearance among mammals of modes of development that depart from the primitive one, we shall first have to answer the question whether the regression of the median rudiment or the formation and strong development of the lateral rudiment is the primary change. The latter supposition can hardly be called in question, since the paired rudiment reveals itself already as processes at the extremities of the semi-arches long before the spinal cord is enclosed completely by the semi-arches, that is long before the median rudiment can manifest itself in the ontogeny. Undoubtedly the primary deviation of the phylogenetically primitive mode of development consists in the appearance during the ontogeny of protuberances at the end of the semi-arches. The more intense the outgrowth of these protuberances into processes constituting the paired rudiment of the processus spinosi, the less will be the part played by the median rudiment in the formation of the spinous processes. When half a spine totally arises from the paired rudiment the median rudiment no longer develops into a separate apex; the median cartilaginous mass does not extend farther than the extremities of the semi-spines (type 4). So far the regression of the unpaired rudiment is to be considered as the immediate consequence of the strong development of the lateral paired rudiment. Apparently the regression of the median rudiment, once begun, can go farther independently; from which ensue the 5th and the 6th types, where, transiently or persistently, the median cartilaginous mass no more extends as far as the extremity of the semi-spines.

The occurrence of the paired lateral spinous process which initiates the new modes of development, depends on a change in the relation of the deep dorsal muscles to the spinous processes. In Amphibians the deep dorsal musculature is still arranged segmentally; the muscle-masses stretch from myoseptum to myoseptum, the processus spinosi are so to say supporting elements of the myosepta. In Reptiles and mammals the conditions are different; the deep dorsal muscles are no longer inserted in the myosepta but in the skeleton of the vertebral column itself, consequently also in the spinous processes. This change shows itself

already in the ontogeny in a typical way. While in Amphibians the dorsal musculature develops quite independently from the skeleton and has already reached the dorsal median line in a stage, in which the cartilage has only been formed in the basal part of the semi-arches, we see that in Reptiles and in mammals the dorso-median extension of the musculature goes on *pari passu* with the growth of the semi-arches round the spinal cord. As soon as the first rudiment of the cartilaginous neural laminae appears, the musculature attaches itself to the semi-arches, above all to their extremities, and thus follows the dorsal extension of the spines. This relation between musculature and extremities of the spines, which appears already early in the ontogeny, gives rise to the development of the terminal protuberances in which the muscles are inserted. The intense development of these protuberances, which represent the paired rudiment of the spinous process, induces regression of the median rudiment. As stated before, this regression must be considered in the beginning as a direct result from the intense development of the lateral rudiment; eventually it can proceed independently; it culminates in the persistence of a bifid neural spine.

My material for the study of the development of the osseus processus spinosi was not quite sufficient. Still, from my observations I may deduce that developmental types can be distinguished that are, in principle, similar to those of the cartilaginous processes. Special mention should be made of the fact that I could establish at some cervical vertebrae, especially at the epistropheus, of some young anthropoids, that the spinous process consists originally of a paired osseous mass. The unpaired condition of the spines in the adult sometimes results from complete coalescence of the halves, sometimes from the development of an unpaired rudiment between and on the previously formed paired, osseous mass. Also the origin of the osseus cervical spines in man which are permanently split at the end, must therefore be ascribed to fetalization.

It should be pointed out at the conclusion of this exposition that on the ground of the described mode of development variations at the cervical spines in man may be expected in two directions.

It may very well be possible that as an atavistic phenomenon the regression of the median mass of cartilage (resp. bone) is not so strong as usual, so that the semi-spines coalesce up to their extremities. Then the unsplit spinous processes appear, which occur very frequently from the 3rd up to and including the 6th cervical process in the lower races, and are not rare also with Europeans.

In the European, however, an unsplit spinous process at the epistropheus is of rare occurrence; among 782 epistrophei of Dutchmen I detected this variation only in 3 cases.

Neither does it appear improbable that the regression of the median mass of bone is stronger than usual, so that the semi-spines do not unite at all and the split reaches as far as the vertebral canal. Among the 782 cases just-mentioned I found this variation in 5 cases. I doubt, however, whether

these are really cases of pure regression of the median rudiment, since with all of them the spinous processes were only little developed, so that perhaps a pathological inhibition of growth and coalescence of the halves may come into play here. I did find, however, this variation 5 times at the first vertebra of the sacrum in man where well developed semi-spines were separated as far as the sacral canal by a narrow slit.

Finally I wish to consider the question, whether RUGE and VON EGGELING are right in assuming a correlation between the terminal bifurcation of the cervical spines in man and the erect attitude of man. As has been set forth in the foregoing the bifurcation results from regression of the median rudiment of a spine which regression has taken place in a different degree among the mammals, and which culminated at the cervical vertebrae of man. Consequently the assumption of the erect attitude cannot possibly be regarded as the real cause of the bifurcation. The question may be propounded, however, whether the erect attitude might have promoted the considerable regression of the median rudiment which at the cervical vertebrae of man has taken place in so high a degree. It seems to me superfluous indeed to seek for a cause why this regression is stronger in man than in all other mammals, since in many other respects man deviates farther than all other mammals from the assumed primitive condition or mode of development. On the other hand there is no repudiating the possibility that the erect attitude has promoted the said regression. The bifid spine is no doubt a less strong attachment for muscles and ligaments than a spine whose halves have grown together up till the end; now it is just with the erect attitude of man that the traction exercised upon the cervical spines by the muscles and especially by the ligaments is less intense than in the quadrupeds. For in man the head balances more or less on the vertebral column, whereas in the quadrupeds the head must be carried by muscles and ligaments, above all by the *ligamentum nuchae*.

Mathematics: — “On the foundations of combinatory Analysis Situs. I. Definitions and elementary theorems.” By M. H. A. NEWMAN, Cambridge. (Communicated by Prof. L. E. J. BROUWER).

(Communicated at the meeting of February 27, 1926.)

In the Encyclopedia article of DEHN and HEEGAARD ¹⁾, published in 1907, a set of definitions was given from which those parts of Analysis Situs which deal essentially with properties of finite collections of objects were to be developed without the use of the ideas and axioms of the Theory of Infinite Aggregates. Such a course is obviously desirable on logical grounds, but serious difficulties have been encountered in actually carrying out the programme indicated by the authors of the article: proofs have not been found, in the intervening years, for a number of theorems which stand at the very beginning of the subject. ²⁾ These difficulties appear to arise rather from the particular definitions adopted in the article than from the nature of the undertaking. In “combinatory” systems of Analysis Situs manifolds are regarded as sets of spherical “cells”, and two manifolds are defined to be “topologically equivalent” or “homoeomorphic” if there is a third manifold which can be obtained from either by a series of modifications of certain prescribed types. The construction of a proof usually reduces, in the more fundamental theorems, to the consideration of the effect of combining, or re-arranging, a series of these steps. In DEHN and HEEGAARD’s system the primitive modification adopted is the *subdivision* of a cell into two cells by any barrier drawn across it. The variety of configurations which can arise from a combination of even two steps of this kind is so great that no classification by mere enumeration can be undertaken; so that from the commencement of the theory recourse must be had to the inductive use of general theorems which would naturally present themselves for investigation at a much later stage, and of which the majority are, in fact, at present unproved.

In the present paper an alternative system of combinatory definitions is proposed. The fundamental transformations (“moves”) are the *addition* and *removal*, instead of the *subdivision*, of cells. This allows the use of

¹⁾ Encykl. der Math. Wiss. III AB 3, *Analysis Situs*.

²⁾ E.g. the “Theorem of Superposition”: *If two manifolds Λ and M , are obtainable from the same manifold by subdivision of its cells, there is a manifold obtainable by subdivision from both Λ and M .* On the difficulties of proceeding from HEEGAARD and DEHN’s definitions to a proof of this theorem cf. E. BILZ, Beiträge zur . . . Analysis Situs, (Math. Zschr. 18 (1923) p. 1.).

simplexes as building units instead of spheres of general character;¹⁾ and the figure directly affected by a single transformation can only have one of a finite number of forms ("primitive clusters").

This paper contains the preliminary analysis of the structure of manifolds, and also some lemmas on primitive clusters, which find their application in the more general theorems of the paper which follows.²⁾

§ 1. Arrays of Simplexes.

If n is a positive integer or zero, an n -dimensional array, or n -array is formed from a finite or enumerable set of objects by specifying which among the groups of $n+1$ objects contained in the set are the *units* of the array. The choice is unrestricted save that every object must belong to at least one unit. The objects are called the *vertices* of the n -array,³⁾ and if $0 \leq k < n$ any $k+1$ vertices all belonging to the same unit form a k -component of the array. An $(n-1)$ -component is called a *face*; units having a face in common are *adjacent*.

An n -simplex is an n -array with only one unit.

The sum, $\Gamma + \Delta + \dots$, of a number of n -arrays, Γ, Δ, \dots , is the n -array whose units are all the units of all the arrays. If Γ contains⁴⁾ Δ , $\Gamma - \Delta$ is the sum of the n -simplexes belonging to Γ but not to Δ .

If S and T are distinct⁵⁾ m - and n -simplexes, ST is the $(m+n+1)$ -simplex containing all the vertices of both. If U is ST , U/S is T (the component of U opposite S). If Γ and Δ are distinct m - and n -arrays, $\Gamma\Delta$ is the sum of all products ST , where S is a unit of Γ , and T of Δ .

(The number n is from this point supposed not less than 1).

An n -array is *regular* if each vertex belongs to only a finite number of units, and each face to only two. It is *connected* if every two units are the extreme members of a chain, i.e. of a finite sequence of units such that adjacent members of the sequence are adjacent units of the array.

The sum of the faces of an n -array, Δ , which belong each to only one unit is the *boundary* of Δ , written $\bar{\Delta}$.

If there are no boundary faces the array is *unbounded*, otherwise it is *bounded*. A component not belonging to the boundary is *internal*, a component belonging to only one unit is *free*.

(If Γ and Δ are unrestricted, an internal component of Γ is not necessarily interior to $\Gamma + \Delta$).

1) Manifolds were first defined as sums of *simplexes*, (regarded as infinite aggregates of points), by L. E. J. BROUWER, "Ueber Abbildungen von Mannigfaltigkeiten", Math. Ann. 71 (1911).

2) These Proceedings, p. 627.

3) The name *points* is reserved for the complex entities which are considered in the theory of continuous manifolds.

4) The k -array Θ is contained in, or belongs to, the n -array Γ only if every unit of Θ is a unit or component of Γ .

5) i.e. having no vertex in common.

1. If Γ and Δ have no common vertex and $d(\Gamma\Delta) > 0$,¹⁾ $\overline{\Gamma\Delta}$ is $\Gamma \cdot \overline{\Delta} + \overline{\Gamma} \cdot \Delta$.

(If S is a unit of Γ , T a unit of Δ , S' a face of S , and T' a face of T , typical faces of $\Gamma\Delta$ are $S'T$ and ST' ; and the condition that, e.g. $S'T$ belongs to no unit of $\Gamma\Delta$ save ST is that S' belongs to no unit of Γ save S).

In order that this theorem may remain true when Γ or Δ is a vertex or is unbounded, it is agreed that when $d(\Phi) = 0$, $\overline{\Phi}$ is to be omitted from all terms containing it, and that when Φ is unbounded all terms containing $\overline{\Phi}$ are to be omitted.

If Γ and Δ are both unbounded, $\Gamma\Delta$ is unbounded.

2. If Γ is a regular, unbounded n -array, there is no n -array, Δ , not contained in Γ , such that $\Gamma + \Delta$ is regular and connected.

(Clear).

3. If $n \geq 2$, the boundary of a regular, bounded n -array is an unbounded $(n-1)$ -array.

Let Γ be the bounded n -array, S_{n-2} an $(n-2)$ -component of $\overline{\Gamma}$, S_{n-1} a boundary face containing it, and S_n the unit of Γ containing S_{n-1} .

If the face of S_n , other than S_{n-1} , which contains S_{n-2} is internal, it belongs to a second unit, T_n , of Γ . If the face of T_n , not belonging to S_n , which contains S_{n-2} is internal, it belongs to a third unit V_n . If any member of the series obtained by continuing in this way recurs, it can only be S_n , and its immediate predecessor contains S_{n-1} , contrary to the hypothesis that S_{n-1} is in the boundary. Hence the series does not recur, but terminates, and its last member contains another boundary face containing S_{n-2} .

§ 2. Topological Equivalence.

If a (1,1) correlation can be established between the vertices of two n -arrays, Γ and Δ , in such a way that the correlates of the vertices of each unit of Γ are the vertices of a unit of Δ , and *vice versa*, the two arrays are *congruent*.

(It is assumed from this point that all the n -arrays considered are *closed*, i. e. that they contain only a finite number of simplexes.)²⁾

Let Γ be a bounded n -array and S an n -simplex, not belonging to Γ . S is said to have *regular contact with Γ* if it is the product of two components, U and V such that

- A (i) U belongs to $\overline{\Gamma}$
- A (ii) U is interior to $UV + \Gamma$
- A (iii) V does not belong to Γ

¹⁾ $d(\Phi)$: "the dimension number of Φ ".

²⁾ The definitions remain significant and most of the theorems remain valid, without this restriction. But it is obvious that to give an adequate account of the equivalence of open n -arrays infinite sequences of "moves" must be admitted; and the investigation of such sequences it is convenient to postpone.

Both U and V must contain at least one vertex.



Regular contact.



Irregular contact.

Fig. 1.

Clearly the faces $U \cdot \bar{V}$ are interior to $\Gamma + UV$, the faces $V \cdot \bar{U}$ are in its boundary.

4. If Γ is regular, those of its boundary faces which contain U form the array $U \cdot \bar{V}$.

For a boundary face of Γ containing U but not belonging to $U \cdot \bar{V}$ would be a boundary face of $\Gamma + UV$, contrary to A (ii); if a unit of $U \cdot \bar{V}$ did not belong to $\bar{\Gamma}$, the set of boundary faces of Γ at U would be a subset of the units of $U \cdot \bar{V}$, and U would therefore be on its boundary. But the boundary of the regular array Γ is unbounded, and therefore U is interior to the set of units of $\bar{\Gamma}$ containing it.

Hence

5. If Γ is regular the common faces of Γ and UV are boundary faces of Γ .

(For they all belong to $U \cdot \bar{V}$).

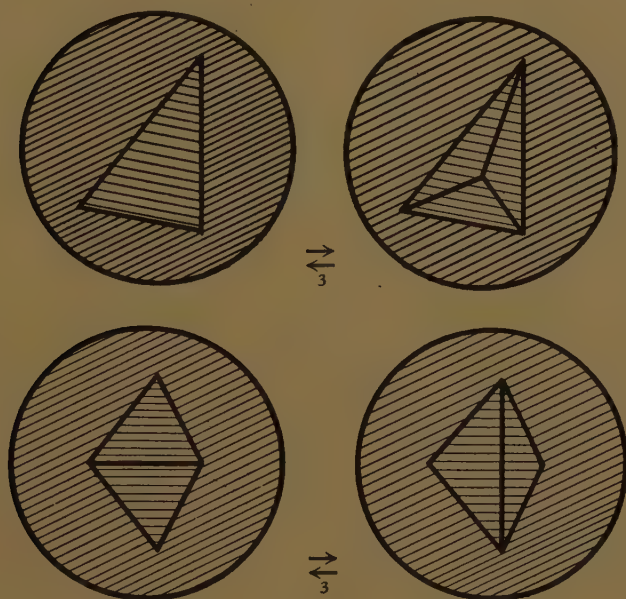
- If Γ is a bounded n -array we define as a *move of type 1* the operation of adding to Γ an n -simplex having regular contact with it; and as a *move of type 2* the operation of removing from Γ an n -simplex, S , having regular contact with $\Gamma - S$.

If X and Y are distinct k - and $(n-k-1)$ -simplexes, $X \cdot \bar{Y}$ and $Y \cdot \bar{X}$ are complementary primitive n -clusters. Their sum is seen to be \overline{XY} .

If Γ is any n -array, and $X \cdot \bar{Y}$ a primitive n -cluster contained in Γ ,

it is a *move of type 3* to replace $X \cdot \bar{Y}$ by its complement, $Y \cdot \bar{X}$, provided that

- $B(i)$ X does not belong to $\Gamma - X \cdot \bar{Y}$
 $B(ii)$ Y does not belong to $\Gamma - X \cdot \bar{Y}$



Moves of type 3.

Fig. 2.

If a *bounded* n -array, Γ , can be transformed by a finite succession of moves, of any or all of the types 1, 2, and 3, into an n -array which is congruent to the n -array Δ , Γ is said to be *topologically equivalent* to Δ , and we write: $\Gamma \rightarrow \Delta$ ¹⁾. "Topologically equivalent" may usually be shortened to "equivalent."

If Γ and Δ are two *unbounded* n -arrays, and units S of Γ , and T of Δ exist, such that $\Gamma - S$ is bounded and topologically equivalent to $\Delta - T$, Γ is said to be *topologically equivalent* to Δ . (It will be shewn later, (24), that in the case of manifolds the property is independent of the choice of S and T).

Equivalence is both *transitive* and *symmetrical*. For if $\Gamma \xrightarrow{1} \Delta$, $\Delta \xrightarrow{2} \Gamma$; and if $\Gamma \xrightarrow{3} \Delta$, $\Delta \xrightarrow{3} \Gamma$.

6. If Γ is a *regular, connected, bounded* n -array, and $\Gamma \rightarrow \Delta$, Δ is a *regular, connected bounded* n -array.

The case $n=1$ is trivial. We therefore suppose $n \geq 2$.

1) " $\Gamma \xrightarrow{pq} \Delta$ " denotes, when Γ and Δ are bounded, that only moves of types p and q need occur in the transformation of Γ into Δ . It is to allow this notation that the unsymmetrical sign \rightarrow is used for equivalence.

It is sufficient to consider the effect of a single move. *Regularity* is clearly not destroyed if the move is of type 2; nor, in virtue of 5, if it is of type 1; nor, by the conditions *B*, if it is of type 3. The *boundary* is unaffected by a move of type 3, and since it is itself unbounded, only a part of it is affected by a move of type 1 or 2. *Connection* could be destroyed only by removing a unit, S_n , which was the only means of connecting in Γ two units, P_n and Q_n , both adjacent to it. But if the removal of S_n is a move of type 2 the common $(n-2)$ -component, S_{n-2} , of P_n and Q_n , being interior to the set of common faces of S_n and $\Gamma - S_n$, is interior to Γ , and therefore a chain of simplexes starting from P_n , all containing S_{n-2} , constructed in the manner described in 3, cannot terminate, and so forms a cycle, whose units include P_n and Q_n . This is incompatible with the hypothesis that P_n and Q_n can be connected only through S_n .

7. If Γ is a regular, connected, unbounded n -array and Δ an equivalent unbounded n -array, then Δ is regular and connected.

We may again suppose that $n \geq 2$. It may be shewn, by an argument similar to that of 6, that the removal of any unit from Γ gives a regular, connected, bounded n -array. There is, therefore, a unit, T , of Δ such that $\Delta - T$ is a regular, connected, bounded n -array. Since Δ is unbounded, all the boundary faces of $\Delta - T$ must be among those of T . But the boundary of the regular array $\Delta - T$ is unbounded. It is therefore identical with \bar{T} , and $(\Delta - T) + T$ is regular, connected and unbounded.

§ 3. Element, Sphere, Cluster.

An n -element is an n -array which is equivalent to an n -simplex. If q is the smallest number of moves in which the element can be transformed into a simplex, the element is said to be of order q .

An n -sphere is an n -array congruent to the boundary of an $(n+1)$ -element¹⁾.

8. E_n is a regular, connected, bounded n -array.

(Follows from 6).

9. $\Sigma_n \cdot \xrightarrow{3} \cdot \bar{S}_{n+1}$.²⁾ For since an $(n+1)$ -element is a regular $(n+1)$ -array, the addition or removal of a simplex with regular contact replaces a primitive n -cluster of the boundary by its complement (5). Conditions *B(i)* and *B(ii)* are satisfied in virtue of 4 and *A(iii)*, or *A(iii)* and 4

¹⁾ The case $n=0$ is included; a 0-element is a vertex, a 0-sphere a pair of vertices. The assumption $n \geq 1$ is, however, still retained in the text which follows. S and T always denote simplexes, E an element and Σ a sphere. If there is a lower index, (as in E_{n-k-1}) it denotes the dimension-number; upper indices are merely distinguishing marks.

²⁾ If Γ and Δ are unbounded $\Gamma \cdot \xrightarrow{3} \cdot \Delta$ means that Δ can be obtained from Γ by a succession of moves of type 3. The dots are to recall the fact that $\Gamma \rightarrow \Delta$ cannot at present be inferred.

according to whether the alteration to the $(n+1)$ -element is of type 1 or type 2. A move of type 3 does not alter the boundary.

10. Σ_n is a regular, connected, unbounded n -array.

(Cf. the proof of 6).

The smallest number of moves of type 3 required for the transformation of an n -sphere into the boundary of an n -simplex is called the order of the n -sphere.

If S_k and Σ_{n-k-1} have no common vertex, $(0 \leq k \leq n-1)$, $S_k \Sigma_{n-k-1}$ is a complete $(n:k)$ -cluster; and if S_k and E_{n-k-1} have no common vertex, $S_k E_{n-k-1}$ is an incomplete $(n:k)$ -cluster.

In both clusters S_k is the core; and Σ_{n-k-1} is the shell of $S_k \Sigma_{n-k-1}$ and E_{n-k-1} of $S_k E_{n-k-1}$.

If $k=0$ the clusters are called complete and incomplete n -stars.

Clearly, a "primitive cluster" is a complete n -cluster.

11. The core of a complete cluster is an internal component; the core of incomplete cluster is in its boundary.

For the face which is the product of the core and an $(n-k-2)$ -component of the shell is interior to, or in the boundary of, the cluster as the $(n-k-2)$ -component is interior to, or in the boundary of the shell.

12. An n -star is an n -element.

a. If the n -star is complete, let a be its core and Σ its shell.

The theorem is true if the shell is the boundary of a simplex. Suppose it true if the shell is of order $q-1$. Let Σ be obtained by a move of type 3 from Σ^* , of order $q-1$. Let Σ be $\Gamma + U \cdot \bar{V}$, Σ^* be $\Gamma + V \cdot \bar{U}$. (If V is a single vertex it may be supposed not to be a).

By hypothesis Γ does not contain U or V . The sum of the units of $a\Sigma^* + UV$ which contain V is therefore $aV \cdot \bar{U} + UV$, i.e., $V \cdot a\bar{U}$, to which V is interior; and U does not belong to $a\Sigma^*$. Hence UV has regular contact with $a\Sigma^*$. Again, since $a\Gamma$ contains neither aU nor V it is a move of type 3 to change $a\Sigma^* + UV$, which is $a\Gamma + V \cdot a\bar{U}$, into $a(\Gamma + U \cdot \bar{V})$, which is $a\Sigma$.

Thus $a\Sigma^* \xrightarrow{1} a\Sigma^* + UV \xrightarrow{3} a\Sigma$, and $a\Sigma$ is an n -element.

b. If the n -star is incomplete, let a be its core and E its shell.

The theorem is true if E is a simplex. Suppose it true when E is of order $q-1$, and let E be obtainable in a single move from E^* , of order $q-1$.

If the move changing E^* into E is of type 3 the arguments of the preceding paragraph are valid. If E is $E^* + XY$, X being interior to E and Y free, aE is $aE^* + aXY$, aX being interior to aE and Y free. Hence $aE^* \xrightarrow{1} aE$ and aE is an n -element. If E is $E^* - XY$, the removal of aXY from aE^* is a move of type 2, and aE is again an element.

13. If an n -simplex and an n -element, (not a simplex) have the same boundary, their sum is an n -sphere.

Let E be the element, S the simplex, and a a new ¹⁾ vertex. a lies

¹⁾ i.e. a vertex not belonging to any of the arrays already under consideration.

in the boundary of the $(n+1)$ -element aE ; it is clearly interior to $aE + aS$; and S does not belong to aE . Hence $a(E + S)$ is an $(n+1)$ -element, and its boundary, $E + S$, an n -sphere.

14. If $\Gamma_n \xrightarrow{3} \Sigma_n$, Γ_n is an n -sphere. We may suppose only one move is required—say the substitution of $U \cdot \bar{V}$ for $\bar{U} \cdot V$. If then Γ_n is $\Delta_n + \bar{U} \cdot V$ and a is a new vertex

$$\begin{aligned} a\Gamma_n &\xrightarrow{1} a\Gamma_n + UV, \\ &\text{is } a\Delta_n + \overline{aU} \cdot V \\ &\xrightarrow{3} a\Delta_n + aU \cdot \bar{V} \\ &\text{is } a\Sigma_n. \end{aligned}$$

But $a\Sigma_n$ is an $(n+1)$ -element, and so, therefore, is $a\Gamma_n$; and its boundary, Γ_n , is a sphere.

15. Every $(n:k)$ -cluster is an incomplete $(n-k-1)$ -cluster.

Let the cluster be $S\Pi$, where Π may be an $(n-k-1)$ -sphere, or $(n-k-1)$ -element, let a be a vertex of S and S' the opposite face. $a\Pi$ is a complete or incomplete $(n-k)$ -star, and therefore an $n-k$ -element. Hence $S\Pi$, which is $S'a\Pi$, is an incomplete $(n:k-1)$ -cluster.

16. Every $(n:k)$ -cluster is an n -element.

(Follows from 15 and 12).

§ 4. Manifolds.

An n -array is an n -manifold if (1) it is connected, and (2) the sum of the units at each vertex is a complete or incomplete n -star ¹⁾. If at each vertex the simplexes form a complete n -star the manifold is *unbounded*; if not it is *bounded*.

It will be shewn that bounded and unbounded n -manifolds are in fact bounded and unbounded n -arrays in the sense already defined. For the present "bounded-manifold" "unbounded-manifold" must be regarded as indivisible phrases.

17. An n -array which can be obtained from an unbounded manifold by a succession of moves of type 3 is an unbounded manifold.

It is sufficient to examine the effect of a single move of type 3. Let M be the manifold, let the substitution of $V \cdot \bar{U}$ for $U \cdot \bar{V}$ be the given move, and let Γ be $M - U \cdot \bar{V}$, Δ be $\Gamma + V \cdot \bar{U}$. Γ , then, contains neither U nor V .

Let a be a vertex of Δ . If a does not belong to M it must be identical with V , and the sum of the simplexes at a is $V \cdot \bar{U}$, a complete n -star. If, on the other hand, all the units of Δ containing a belong to M , the units at a in Δ are identical with the units at a in M , which form a complete n -star. Suppose then that a belongs to $V \cdot \bar{U}$ but is not V .

(a). Let V be aV' . Of the units of $U \cdot \bar{V}$ in M , the subset $aU \cdot \bar{V}'$ con-

¹⁾ The name "manifolds" is usually given to the arrays here called "unbounded manifolds", but as bounded manifolds appear to play the more important part in the present theory, this unsymmetrical nomenclature is not adopted.

tains α . The set of simplexes at α in M has therefore the form $\alpha(\Delta + U.\overline{V'})$, where $\Delta + U.\overline{V'}$ is an $(n-1)$ -sphere. Neither V' nor U belongs to Δ , or V or U would belong to $\alpha\Delta$, and therefore to Γ . Hence $\Delta + U.\overline{V'} \xrightarrow{3} \Delta + V'.\overline{U}$ which is therefore also a sphere. The array $\alpha\Delta + U.\overline{V}$ in M , which includes all units of M containing α , is replaced in Δ by $\alpha\Delta + V.\overline{U}$ which is $\alpha(\Delta + V'.\overline{U})$. This is therefore the set of simplexes at α in Δ , and, its boundary being a sphere, is a complete star.

(b). If U is $\alpha U'$, all the units of $U.\overline{V}$ belong to the n -star at α in M , which is of the form $\alpha(\Delta + U'.\overline{V})$. This is replaced in Δ by $\alpha\Delta + V.\overline{U}$ and the sum of the units at α in Δ is therefore $\alpha(\Delta + V.\overline{U})$. It follows as before that this is an n -star.

Hence

18. Every n -sphere is an unbounded n -manifold.

19. The n -simplexes at a k -component of an unbounded n -manifold form a complete $(n:k)$ -cluster.¹⁾

The theorem is true when $k=0$. Suppose it true when $k \leq j-1$, where $1 \leq j \leq n-1$. Let S be a j -component of the manifold, α a vertex of S , and S' the opposite face.

The n -simplexes at S' form a certain $(n:j-1)$ -cluster, say $S'\Sigma$. The n -simplexes at S are those units of $S'\Sigma$ which contain α . Since α does not belong to S' , it belongs to Σ , and (18) the units of Σ containing it form an $(n-j)$ -star, $\alpha\Sigma'$. Hence the simplexes at S form the array $S'.\alpha\Sigma'$, which is a complete $(n:j)$ -cluster.

In particular, the n -simplexes containing a face of the manifold form a complete $(n:n-1)$ -cluster i.e. a pair of simplexes. The "unbounded-manifold" is therefore in fact a regular unbounded n -array.

20. If the units of a primitive cluster contained in an unbounded n -manifold are removed, one by one, in any order, all the contacts after the first are regular.

It is sufficient to shew that if M is an unbounded manifold containing $U.\overline{\alpha V}$, UV has regular contact with $M - U.\overline{\alpha V}$.

We first notice that all units of M containing U belong to $U.\overline{\alpha V}$. For if not, $\overline{\alpha V}$ would be drawn on²⁾ the shell of the complete cluster at U ; and this is impossible, for one sphere cannot be drawn on another. (Cf. 2).

Consider the contact of UV with $M - U.\overline{\alpha V}$. The boundary of $M - U.\overline{\alpha V}$ contains $\overline{\alpha V}$, and therefore V ; U does not belong to $M - U.\overline{\alpha V}$; and V , which is interior to M and does not belong to $\alpha U.\overline{V}$, is interior to $M - \alpha U.\overline{V}$, which is $M - U.\overline{\alpha V} + UV$. The contact is regular and $M - U.\overline{\alpha V} + UV \xrightarrow{2} M - U.\overline{\alpha V}$.

¹⁾ Cf. H. KNESER, Ein Topologischer Zerlegungssatz. (These Proceedings 27, (1924) p. 603).

²⁾ " Γ is drawn on Δ " means that the units of Γ form a subset of the units of Δ . It implies that $d(\Gamma) = d(\Delta)$ and that Γ is not Δ .

21. If M is unbounded and $M \xrightarrow{3} \Lambda$, then $M \rightarrow \Lambda$.

It is sufficient to examine the effect of a single move, say the substitution of $V.\bar{U}$ for $U.\bar{V}$. Let S be a unit of $U.\bar{V}$, T a unit of $\bar{U}.V$. If the units of $U.\bar{V}-S$ are removed from $M-S$ in any order, the contacts are all regular: i.e. $M-S \xrightarrow{2} M-U.\bar{V}$. Λ is also an n -manifold, and therefore $\Lambda-T \xrightarrow{2} \Lambda-V.\bar{U}$; i.e. $\Lambda-V.\bar{U} \xrightarrow{1} \Lambda-T$. Since $M-U.\bar{V}$ is $\Lambda-V.\bar{U}$ this is the required result¹⁾.

22. If an n -simplex is removed from an n -sphere the remainder is an n -element.

Sketch of the proof. In extending the range of this theorem from spheres of order $q-1$ to the sphere Σ , of order q , the crux is the case when S , the simplex to be removed, belongs to the new cluster, $V.\bar{U}$, in Σ . If then T is any unit of $U.\bar{V}$ it can be shewn, as in 21, that $\Sigma-S$ can be obtained by moves of types 1 and 2 from the n -element Σ^*-T , where Σ^* is $\Sigma-V.\bar{U}+U.\bar{V}$.

24. If S and T are any two units of an unbounded n -manifold, M , $M-S \rightarrow M-T$.

It is sufficient to examine the case in which S and T have a common face. But in that case $S+T$ is a primitive cluster and therefore, (Cf. 20), $M-S \rightarrow M-(S+T) \rightarrow M-T$.

25. An n -dimensional bounded manifold is a bounded n -array whose boundary is one or more unbounded $(n-1)$ -manifolds.

It follows easily from 11 that the set of boundary vertices is identical with the set of vertices at which the simplexes form an incomplete star. The boundary faces at any boundary vertex, a , are those boundary faces of the incomplete n -star at a which contain a . They are obtained by joining a to the boundary of the shell of the n -star and therefore form a complete $(n-1)$ -star.

26. If Γ is a bounded manifold, conditions $A(i)$ and $A(ii)$ governing regular contact may be replaced by: $A(iiia)$ $U.\bar{V}$ belongs to $\bar{\Gamma}$.

If, condition $A(iiia)$ being satisfied, U were not interior to $\Gamma+UV$, there would be boundary faces of Γ containing U , but not belonging to UV and therefore not contained in $U.\bar{V}$; i.e. the complete $(n-1:k)$ -cluster $U.\bar{V}$ would be contained in another complete $(n-1:k)$ -cluster, which is impossible.

27. If $\Gamma+UV$ is a bounded manifold, the conditions $A(i)$ and $A(iii)$ governing regular contact may be replaced by: $A(iiia)$, $V.\bar{U}$ belongs to $\bar{\Gamma}+UV$. (Cf. 26).

28. If all the units of an n -element have a common vertex, the element is an n -star.

If the common vertex, ξ , is interior to the element, the truth of the theorem is obvious. If it is in the boundary, the array is formed by

¹⁾ We may now drop the dots and write $M \xrightarrow{3} \Lambda$. The symbols $M \xrightarrow{1} \Lambda$, $M \xrightarrow{1,2} \Lambda$ etc., are not used when Λ and M are unbounded.

joining ξ to those boundary faces which do not contain it. It is therefore sufficient to shew that if an $(n-1)$ -star is removed from an $(n-1)$ -sphere the remainder is an $(n-1)$ -element. In this form the theorem is clearly true of the boundary of an n -simplex. The proof that it can be extended to spheres of order q involves considerations similar to those which arose in proving 12 and 17, and may be omitted.

29. An n -array which is equivalent to a bounded n -manifold is a bounded n -manifold.

The theorem is true when $n=1$. Suppose it true when $n \leq m-1$, where $m \geq 2$. From this hypothesis there follow:

30. ($n \leq m-1$). An n -element is a bounded n -manifold.

31. ($n \leq m$). The n -simplexes at a k -component of a bounded n -manifold form an $(n:k)$ -cluster, complete or incomplete, as the k -component is, or not, internal.

This is true when $k=0$. Suppose it is known to follow from the inductive hypothesis if $n < m$, and also if $n=m$ and $k \leq j-1$, where $1 \leq j \leq n-1$.

a. Let S be a boundary j -component, S' a face of S , a the opposite vertex.

The simplexes at S are those units of the $(n:j-1)$ -cluster (say $S'E$) at S' , which contain a . a belongs to E and is on its boundary; for if it were interior to E , aS' would be interior to ES' and therefore to the manifold. Since the element E , (of less than m dimensions) is a bounded manifold, those of its units which contain a form an incomplete $(n-j)$ -star, aE' . The n -simplexes at S therefore form the incomplete $(n:j)$ -cluster $S'a.E'$.

b. Let S be an internal j -component, and S' and a a face and opposite vertex.

If S' is internal, the arguments used in 19 apply. If not, and the $(n:j-1)$ -cluster at S' is $S'E$, a is now interior to E . For if not, S would be in the boundary of $S'E$, and therefore, since this array includes all units of the manifold containing S , in the boundary of the manifold. The units of E containing a therefore form a complete $(n-j)$ -star $a\Sigma'$, and the simplexes at S the complete $(n:j)$ -cluster, $S\Sigma'$.

In particular the array at an internal face is a pair of simplexes. A bounded manifold is therefore a regular array.

The sum of the units of a manifold M which contain a component S will be called "the S -cluster in M ."

32. ($n \leq m$). An incomplete n -star is a bounded manifold.

If the star is aE , and β is a vertex of E , the units of E at β form a complete or incomplete star, $\beta\Pi$. Hence the units of aE at β form the set $\alpha.\beta\Pi$, or $\beta.\alpha\Pi$, and $\alpha\Pi$ is an $(n-1)$ -element.

33. ($n \leq m$). If M is an n -manifold, a component of M interior to a subset, Γ , of M is interior to M and does not belong to $M-\Gamma$.

The component, S , is interior to Δ , the set of units of Γ which contain it. Δ is contained in the S -cluster in M , and therefore can only

have S as an internal component, if the S -cluster in M is a complete cluster and coincides with Δ .

Proof of 29. It must be shewn that an alteration of any of the three types to a bounded m -manifold leaves it a bounded m -manifold.

The effect of a move of type 3 has been discussed in the proof of 17.

Consider the effect of *adding* to the manifold, M , a simplex UV , U being interior to $M + UV$ and V free.

If U is a vertex, the boundary of the shell of the U -star in M coincides with \bar{V} . The boundary of the array at U in $M + UV$ is therefore (13) a sphere, and the array itself an m -star.

If V is a vertex the V -cluster is UV .

If α is a vertex of U but is not identical with it, let U be $\alpha U'$. The contact of UV with αE , the α -star in M , is regular. For all the units of $U \cdot \bar{V}$ contain α , and therefore belong to αE . Since they belong (by hypothesis) to \bar{M} , they belong (33) to $\overline{\alpha E}$; V does not belong to M , much less to αE ; and αE is a bounded manifold (32). Hence (26) $\alpha E + UV$ is an m -element and therefore an incomplete m -star.

Finally, consider a vertex, β , of V . Let V be $\beta V'$. If V' belonged to βE^* , the β -star in M , it would belong to E^* and therefore V would belong to βE^* , which is contrary to hypothesis. $U \cdot \bar{V}$ is $U\beta \cdot \bar{V}' + UV'$, and therefore the array $U\beta \cdot \bar{V}'$ belongs to $\overline{\beta E^*}$. Hence the contact of UV with βE^* is regular, and the set at β in $M + UV$ is an incomplete m -star.

Thus at all vertices of $M + UV$ the simplexes form a star: the sum is a manifold.

The case of the *removal* of a simplex is similar.

34. *The removal of a unit from an unbounded n -manifold leaves a bounded n -manifold.*

(Follows from 22).

35. *An n -array which is equivalent to an unbounded n -manifold is an unbounded n -manifold.*

(Follows from 34 and 13).

§ 5. Some lemmas on Primitive Clusters.

If Γ and Δ are two n -arrays, we write

$$\Gamma \xrightarrow[p, q]{} \Delta, \quad [\text{not } P, Q, \dots]$$

for the statement: "If Φ is any n -array, containing no unit of Γ or Δ , then $\Phi + \Gamma \rightarrow \Phi + \Delta$ provided none of P, Q, \dots is a component of Φ ".

36. *If P, Q, R are three simplexes with no common vertex*

$$P \cdot \bar{Q} \cdot \bar{R} \xrightarrow{3} Q \cdot \bar{P} \cdot \bar{R}, \quad [\text{not } P, Q]$$

If R is a vertex the theorem is reduced to $P \cdot \bar{Q} \xrightarrow{3} Q \cdot \bar{P}$ [not P, Q],

which is true. Suppose its truth is known if $d(R) < q$. Let R be $R'\xi$, R' having $q-1$ dimensions.

$$\begin{aligned}
 P \cdot \bar{Q} \cdot \bar{R} & \text{ is } P\xi \cdot \bar{Q} \cdot \bar{R}' + PR' \cdot \bar{Q}, \\
 & \xrightarrow{3} Q \cdot \bar{P}\xi \cdot \bar{R}' + PR' \cdot \bar{Q}, & [\text{not } Q, P\xi], \\
 & \text{ is } P \cdot \bar{Q}R' + \xi Q \cdot \bar{P} \cdot \bar{R}', \\
 & \xrightarrow{3} QR' \cdot \bar{P} + \xi Q \cdot \bar{P} \cdot \bar{R}', & [\text{not } QR', P], \\
 & \text{ is } Q \cdot \bar{P} \cdot \bar{R}.
 \end{aligned}$$

The four conditions, $[\text{not } P, P\xi, Q, QR']$ are clearly contained in $[\text{not } P, Q]$.

Noticeable special cases are:

$$P \cdot \bar{R} \xrightarrow{3} \alpha \cdot \bar{P} \cdot \bar{R} \quad [\text{not } P, \alpha], \quad . \quad . \quad . \quad . \quad (1)$$

$$\beta \cdot \bar{R} \xrightarrow{3} \alpha \cdot \bar{R}, \quad [\text{not } \beta, \alpha], \quad . \quad . \quad . \quad . \quad (2)$$

The value of the last result is that it shews that the transformation need not proceed by way of $\beta \cdot \bar{R} \rightarrow R$, which would require $[\text{not } R]$.

The following generalization of 36 is easily proved.

37. If P, Q, R, \dots, S are any number of simplexes, no two having a common vertex, then

$$P \cdot \bar{Q} \cdot \bar{R} \dots \bar{S} \xrightarrow{3} Q \cdot \bar{P} \cdot \bar{R} \dots \bar{S}, \quad [\text{not } P, Q].$$

It is convenient to prove together the following four theorems:

38. If the common part¹⁾ of an n -manifold, M , and a primitive n -cluster, $S \cdot \bar{T}$, is an $(n-1)$ -element belonging to the boundaries of both, then $M \xrightarrow{1} M + S \cdot \bar{T}$.

(In 39–44 U and V are opposite components of an $(n+2)$ -simplex and M a bounded n -manifold drawn on \bar{U}, \bar{V}).

39. If U' is a face of U and Γ the set of units of $U' \cdot \bar{V}$ which do not belong to M , then $M \xrightarrow{1} M + \Gamma$, provided $M + \Gamma$ is not $\bar{U} \cdot \bar{V}$.

40. If no face of U is interior to M at least one face of V does not belong to M ($d(V) > 0$).

41. If an h -component, X , but no $(h-1)$ -component of U is interior to M , there is a face, V' , of V such that $(U/X) \cdot V'$ does not belong to M . ($d(V) > 0$).

The four theorems are clearly true if $n=1$. Suppose them true if $n \leq m-1$. From this assumption there follow:

42. ($n \leq m-1$). M is an n -element.

For to each vertex, ξ , of U corresponds an array Γ_ξ , (which may in some cases have no units), consisting of the units of $(U/\xi) \cdot \bar{V}$ which do not belong to M . The arrays Γ_ξ can, by 39 Hyp., be added to M in

¹⁾ Θ is the common part of Γ and Δ means that the common units, (if any), and common components of Γ and Δ are the units and components of the array Θ .

succession, by moves of type 1, until only one of those which actually have units remains. This remaining array, Γ_n , being part of $(U/\eta) \cdot \bar{V}$ is a primitive cluster, and the array that has been obtained from M , being the remainder of $\bar{U} \cdot \bar{V}$, is an n -element. M itself is therefore also an n -element.

43. ($n \leq m-1$). If an n -element is removed from $\bar{U} \cdot \bar{V}$ the remainder is an n -element.

(During the process described in 42 the simplexes added, by moves of type 1, to M are removed, by moves of type 2, from $\bar{U} \cdot \bar{V} - M$ and the final result — one of the arrays Γ_ξ — is an n -element).

44. ($n \leq m-1$). If U' is any face of U , and Δ the set of units of $U' \cdot \bar{V}$ belonging to M , $M \xrightarrow{2} M - \Delta$, provided M is not Δ .

Proof of 38. Suppose n equal to m and let $d(S) = k$. If $k = m$ the theorem is reduced to 26. Suppose then that the theorem is true if $n = m$ and $k \geq j+1$, where $j \leq m-1$, and that in the given case $n = m$ and $k = j$. Let E be the common boundary element.

If no component of S is interior to E there is a face, T' , of T which does not belong to E , (40); and the array $S \cdot \bar{T} - S \cdot T'$, (i.e., if ξ is T/T' , the array $\xi S \cdot \bar{T}'$, which is a primitive $(m:j+1)$ -cluster), has also the array E in common with M . Its units may therefore be added to M by moves of type 1. The remaining simplex, ST' , has regular contact with $M + \xi S \cdot \bar{T}'$. For S is interior to $S \cdot \bar{T}$ and T' belongs neither to $\xi S \cdot \bar{T}'$ nor, by hypothesis, to M .

If an h -component, U , but no $h-1$ -component of S is interior to E , let S be UV . There is then a face, T' of T , such that VT' does not belong to E . If ξ is T/T' , the common part of M and $\xi S \cdot \bar{T}'$ is an $(m-1)$ -element. The common faces, being those units of E which do not belong to $T' \cdot \bar{S}$, certainly form an $(m-1)$ -element (44). Suppose then that M and $\xi S \cdot \bar{T}'$ have a common component, W , which does not belong to a common face; from the conditions governing the contact of M and $S \cdot \bar{T}$, W must belong to a common boundary face of M and ST' . \bar{ST}' is $S \cdot \bar{T}' + VT' \cdot \bar{U} + UT' \cdot \bar{V}$; the units of $S \cdot \bar{T}'$ are interior to $S \cdot T$, those of $VT' \cdot \bar{U}$ all contain VT' which we have supposed not to belong to E , and therefore $UT' \cdot \bar{V}$ contains all units of E which belong to ST' . Also the part of the boundary of $S \cdot \bar{T}$ belonging to $\xi S \cdot \bar{T}'$ is $S \cdot \bar{T}'$, i.e. $UV \cdot \bar{T}'$. Thus W must be a component of both $UT' \cdot \bar{V}$ and $UV \cdot \bar{T}'$ and therefore of their set of common faces, $U \cdot \bar{T}' \cdot \bar{V}$, which belongs to the U -cluster in $\bar{S} \cdot \bar{T}$. But since U is, by its definition, interior to E , the whole of the U -cluster in $\bar{S} \cdot \bar{T}$ belongs to E and therefore those units of the boundary of $\xi S \cdot \bar{T}'$ which contain $U \cdot \bar{T}' \cdot \bar{V}$ belong to M . The hypothesis that W does not belong to a common face of M and $\xi S \cdot \bar{T}'$ is untenable.

Thus the primitive cluster $\xi S \cdot \bar{T}'$ satisfies the conditions of the theorem; its units can by the inductive hypothesis be added to M by moves of

of type 1; and ST' has regular contact with $M + \xi S, \overline{T'}$: for VT' does not belong to M , and U is interior to $M + S, \overline{T}$.

Proof of 39. Let $n=m$. In view of 38 and 42 it is sufficient to shew that the common part of M and Γ is a bounded $(m-1)$ -manifold. It is convenient to prove the slightly more general result that if M^* and Γ^* are as M and Γ in 39 save that $M^* + \Gamma^*$ may be $\overline{U}, \overline{V}$, the common part of M^* and Γ^* is an $(m-1)$ -manifold. Let this be assumed true when $\overline{U}, \overline{V}$ is replaced by the boundary of a primitive cluster of lower dimensions. Let Q be any common component of Γ^* and M^* , let U' be $P_1 Q_1$,¹⁾ V be $P_2 Q_2$, Q be $Q_1 Q_2$. Then U', \overline{V} is $P_1 Q, \overline{P_2} + P_1 Q_1 P_2, \overline{Q_2}$ so that the Q -cluster in Γ^* is contained in $P_1 Q, \overline{P_2}$. Again, if ξ is U/U' , the Q -cluster in M^* is contained in $Q, \overline{\xi P_1}, \overline{P_2}$, the Q -cluster in $\overline{U}, \overline{V}$. The shell, Γ' , of the Q -cluster in Γ^* is then an element drawn on $\overline{\xi P_1}, \overline{P_2}$, consisting of all those units of $P_1, \overline{P_2}$ which do not belong to M' , the shell of the Q -cluster in M^* . Hence by the inductive hypothesis the common components of M' and Γ' form an $(h-1)$ -manifold, Π_{h-1} (where $h = d(\Gamma') = d(M')$). Since $h < m$, Π_{h-1} , which is drawn on, or identical with, $\overline{\Gamma'}$, is a sphere or an element (42). The common components of M^* and Γ^* containing Q form the array $Q \Pi_{h-1}$, a complete or incomplete cluster. This establishes the subsidiary theorem, concerning M^* and Γ^* , and as it is clear that the common array of M and Γ is a proper part of $\overline{\Gamma}$ it must be a bounded $(m-1)$ -manifold, and the truth of 39 follows.

Proof of 40. Let $n=m$. Using the theorems which have now been proved, 40 can be enunciated in the symmetrical form:

If $\overline{U}, \overline{V}$ is the sum of two elements, E_1 and E_2 , either a face of U is interior to E_1 , or a face of V is interior to E_2 .

It is therefore sufficient to consider the case in which $d(V) \leq d(U)$. The theorem is clearly true if $d(U) = 0$. We therefore suppose U has at least two vertices.

If there were a vertex, ξ , of U which did not belong to E_1 , E_1 would be contained in $(U/\xi), \overline{V}$; and if, in this case, U/ξ were not interior to E_1 , there would be a face, V^1 , of V , such that $(U/\xi), V^1$, and therefore V^1 itself, did not belong to E_1 . We may therefore assume that if ξ is any vertex of U , ξ belongs to E_1 but is not interior to it.

Let U be ξU^1 , and let ξe_1 be the ξ -star in E_1 . Since $\xi, \overline{U^1}, \overline{V}$ is the ξ -star in $\overline{U}, \overline{V}$, e_1 is an element drawn on $\overline{U^1}, \overline{V}$. No face of U^1 is interior to e_1 ; for if it were, a face of U would be interior to ξe_1 , i. e. to E_1 . Hence by the inductive hypothesis there is at least one face of V , say V^1 , which does not belong to e_1 . $U^1 V^1$ is the only unit of $\overline{U}, \overline{V}$ which contains V^1 but not ξ , and therefore is the only unit of E_1 containing V^1 . Thus if every face of V belonged to E_1 , there would correspond to every vertex, ξ , of U , a vertex, η , of V such that $(UV)/(\xi\eta)$ is the only

¹⁾ On this page suffixes are used (for typographical reasons) as distinguishing marks, not dimension numbers.

unit of E , containing V/η . Clearly, in this correlation, the same vertex of V cannot correspond to two different vertices of U and therefore if $d(V) < d(U)$ the hypothesis that every face of V belongs to E is untenable. If $d(U) = d(V)$ the only possibility to be considered is that

E_1 is $\sum \left(\frac{UV}{\xi\eta} \right)$, each vertex of U and V appearing in one term only

of the sum. But this array is clearly not an element, for no two units have a common face. The hypothesis that every face of V belongs to E_1 must therefore be abandoned.

Proof of 41. Let U be XY . The trivial or degenerate cases in which X is a vertex, or Y does not belong to M , may be excluded. Y cannot be interior to M , or M would contain the whole of $\bar{U} \cdot \bar{V}$. The Y -cluster in M is then Ye , where e is an element drawn on $\bar{X} \cdot \bar{V}$. If a face, X' , of X were interior to e , the $Y \cdot X'$ -cluster in M would be the whole of $X' \cdot Y \cdot \bar{V}$. Since, (X being interior to M) the X -cluster in M is $X \cdot \bar{Y} \cdot \bar{V}$ the X' -cluster in M would in this case contain the sum of these two arrays, viz., $X' \cdot \bar{\alpha Y} \cdot \bar{V}$ where α is X/X' . But this is the whole of the X' -cluster in $\bar{U} \cdot \bar{V}$, and cannot, owing to the conditions imposed on X , belong to M . There is therefore no face of X interior to e ; by the inductive hypothesis at least one unit of \bar{V} does not belong to e , and therefore at least one unit of $Y \cdot \bar{V}$ does not belong to Ye , the Y -cluster in M .

45. If $S \cdot \bar{T}$ is drawn on an n -manifold, M , and the components of $S \cdot \bar{T}$ belonging to \bar{M} form a bounded $(n-1)$ -manifold, then $M \xrightarrow{2} M - S \cdot \bar{T}$.

(The proof is similar to that of 38).

From 38 and 45 we obtain the following generalisation of the rules governing regular contact with manifolds, (cf. 26 and 27).

46. If

$C(ii) \ U \cdot \bar{V} \cdot \bar{W}$ is drawn on \bar{M} ,

$C(iii) \ V$ does not belong to M ,

then

$$M \xrightarrow{1} M + UV \cdot \bar{W}.$$

Every component of $UV \cdot \bar{W}$ which does not belong to $U \cdot \bar{V} \cdot \bar{W}$ contains or is contained in V , and therefore the components common to M and $UV \cdot \bar{W}$ form the array $U \cdot \bar{V} \cdot \bar{W}$ itself, which is an $(n-1)$ -element.

47. If $UV \cdot \bar{W}$ is drawn on M and

$D(ii) \ U$ is interior to M ,

$D(iia) \ V \cdot \bar{U} \cdot \bar{W}$ belongs to \bar{M} ,

then

$$M \xrightarrow{2} M - UV \cdot \bar{W}.$$

(From 45).

Mathematics. — "*On the foundations of combinatory Analysis Situs.*
 II. *Theorems on sets of elements.*" By M. H. A. NEWMAN.
 (Communicated by Prof. L. E. J. BROUWER).

(Communicated at the meeting of February 27, 1926).

This paper contains, first, an investigation of the extent to which moves of one type can be replaced by moves of other types, and secondly, some theorems on manifolds considered as sums of elements¹⁾

In section I it is shewn that if A and M are equivalent bounded manifolds, then $A \xrightarrow{12} M$ (Theorem 1); $A \xrightarrow{13} M$, (Theorem 3a); and $A \xrightarrow{23} M$, (Theorem 3b); that if A and M are equivalent unbounded n -manifolds $A \xrightarrow{3} M$, (Theorem 5); and that if E^1 and E^2 are n -elements with a common boundary, $E^1 \xrightarrow{3} E^2$, (Theorem 4). The only other relations whose possibility is plausible are: (1) If A and M are equivalent bounded manifolds with a common boundary, then $A \xrightarrow{3} M$; and (2) If E is an n -element and S an n -simplex, then $E \xrightarrow{2} S$. Whether the first of these assertions is true I do not know, but the second is certainly false. If $n > 2$ an n -dimensional element can be constructed from which no simplex can be removed by a move of type 2.

In section II theorems are proved on the effect of adding elements to elements, and elements to manifolds, and finally a theorem, (Theorem 10), on the structure of manifolds in terms of general elements instead of simplexes. From this theorem it can be deduced that if two equivalent manifolds, according to the DEHN-HEEGAARD definitions, are divided into simplexes, they are equivalent in the sense of the present papers; so that the new definitions lead to no loss of generality.

From this point it is not difficult to construct a proof of the "Theorem of Superposition" mentioned on p. 611; but this theorem no longer arises naturally at the outset and its proof is reserved for a subsequent paper²⁾.

I. Relations between moves of the three types.

§ 1. Replacement of Moves of Type 3.

The following two lemmas will be proved together.

Lemma 1. If S is a boundary component of an n -manifold, M , such that the units of \bar{M} at S form the array $S\Sigma \cdot \bar{T}$, then, provided T does not belong to M , $M \xrightarrow{12} M + S\Sigma T^3$.

¹⁾ The definitions are those of the preceding paper. The n^{th} theorem of that paper is denoted by $1n$.

²⁾ A proof will be published shortly in the Lond. Math. Soc. Proceedings.

³⁾ The conventions of the preceding paper as to the meaning of letters are retained.

Lemma 2. If T is a boundary component of an n -manifold, M , such that the units of M at T form the array $S\Sigma T$, then, provided S is interior to M , $M \xrightarrow{12} M - S\Sigma T$.

(S and T must each contain at least one vertex, but Σ may be absent).

(The first object of the proof of Lemma 1 is so to modify M that the S -cluster in the boundary becomes $S\Sigma^*T$, where Σ^* is a sphere of lower order than Σ . The simplest moves by which this is formally possible are not always regular. We therefore first modify the manifold so that a new S -cluster in \bar{M} congruent to $S\Sigma T$ is obtained. The new manifold, (that called $M^{(1)}$ in the proof), can in all cases be altered so that the S -cluster in its boundary has the desired form $S\Sigma^*.T$ and, by an inductive hypothesis, $S\Sigma^*T$ can then be added. In the remainder of the proof the added array is transformed into $S\Sigma T$).

In both lemmas, if $d(S) = n-1$, Σ must be absent, and T a vertex. The lemmas are then true by the definitions. Suppose then that they are true if $d(S) > j$. (Hyp. a).

In both lemmas, if $d(T) + d(S) = n-1$, Σ must be absent and the lemmas are reduced to I 26 and I 27. Suppose then that they are true if $d(S) = j$ and $d(T) > h$. (Hyp. b).

Both lemmas are true if Σ is of order zero, for they are then reduced to I 46 and I 47. We suppose then, finally, that the lemmas are true if $d(S) = j$ and $d(T) = h$, provided Σ is of order less than q . (Hyp. c.).

In the given case let $d(S) = j$, $d(T) = h$ and let Σ be obtainable by a move of type 3 from a sphere, Σ^* , of order $q-1$. Let \mathcal{S} be $\Gamma + U.V$, Σ^* be $\Gamma + V.U$. We first suppose V is not a vertex. Let α be any of its vertices, V' the opposite face, and let Π be $\Pi + \alpha\Psi$, where Π does not contain α . Thus \mathcal{S} is $\Pi + \alpha(\Psi + U.V') + UV'$.

The αS -cluster in \bar{M} is $\alpha S.T(\Psi + U.V')$ and therefore (replacing T by a new vertex, β , in Hyp. a)

$$M \xrightarrow{12} M + \beta . \alpha S . \bar{T}(\Psi + U.V').$$

Let the manifold on the right be called $M^{(1)}$. The contact of the array $SU.\beta V'.\bar{T}$ with $M^{(1)}$ satisfies the conditions C(iiia) and C(iii) (I 46). For the S -cluster in $\bar{M}^{(1)}$, viz., $ST(\Pi + U.\beta V' + \beta\Psi)$, contains $SU.T.\beta V'$; and $\beta V'$ could only belong to $M^{(1)}$ if it belonged to one of the added simplexes, which is clearly not the case. Hence

$$M^{(1)} \xrightarrow{1} M^{(1)} + \beta SUV'.\bar{T},$$

which we call $M^{(2)}$. The S -cluster in $\bar{M}^{(2)}$ is $S.T(\Pi + \beta\Psi + \beta V'.U)$, which is congruent to $S.T(\Gamma + V.U)$. Hence, using Hyp. c.,

$$M^{(2)} \xrightarrow{12} M^{(2)} + ST(\Pi + \beta\Psi + \beta V'.U),$$

$$\text{is } M + SV'\beta.U\bar{T} + ST(\Pi + \beta\Psi) + \alpha\beta S.T(\Psi + U.V'),$$

$$\text{is } M + SV'\beta.U\bar{T} + \Omega, \text{ say.}$$

which we call $M^{(3)}$. Only the second term in this expression contains $V'\beta$. Hence $V'\beta$ is in the boundary of $M^{(3)}$ and the units of $\overline{M^{(3)}}$ containing it are $V'\beta \cdot \overline{S \cdot UT}$. Also, the S -cluster in $\overline{M^{(2)}}$ being identical with the S -cluster in $\overline{M^{(3)} - M^{(2)}}$, S is interior to $M^{(3)}$.

It follows (I 47) that

$$M^{(3)} \xrightarrow{2} M + \Omega.$$

Since S is internal to $M^{(3)}$, the S -cluster in $\overline{M + \Omega}$ is identical with that in the boundary of the array, $SV'\beta \cdot \overline{UT}$, which has just been removed, viz. $S \cdot \overline{UT} \cdot \overline{V'\beta}$; and UT does not belong to $M + \Omega$. Hence

$$M + \Omega \xrightarrow{1} M + \Omega + SUT \cdot \overline{V'\beta}$$

which we call $M^{(4)}$.

$$M^{(4)} \text{ is } M + ST(\Pi + UV') + \alpha\beta S \cdot \overline{T}(\Psi + U \cdot \overline{V'}) + S\beta T(\Psi + U \cdot \overline{V'}).$$

The last term of this expression contains all the simplexes of $M^{(4)}$ of which βT is a component; and S is interior to $M^{(4)}$. Hence, (Hyp. b, concerning Lemma 2),

$$M^{(4)} \xrightarrow{12} M^{(4)} - S\beta T(\Psi + U \cdot \overline{V'}).$$

The simplexes $\alpha\beta S \cdot \overline{T}(\Psi + U \cdot \overline{V'})$ are now the only remaining units which contain β . They can therefore be removed, by moves of types 1 and 2, by reversing the series of moves by which they were added to M . This gives

$$M^{(4)} \xrightarrow{12} M + ST(\Pi + U \cdot V').$$

The S -cluster in the boundary of this manifold is identical with the S -cluster in the boundary of the array, $\beta S \cdot \overline{\alpha T}(\Psi + U \cdot \overline{V'})$, which has been removed from $M^{(4)}$, and is therefore $S \cdot \overline{\alpha T}(\Psi + U \cdot \overline{V'})$. Hence, by a final use of Hyp. b., concerning Lemma 1, we find

$$M^{(4)} \xrightarrow{12} M + ST(\Pi + UV') + S\alpha T(\Psi + U \cdot \overline{V'})$$

which is $M + ST\Sigma$.

Lemma 1 is thus extended to the case when Σ is order q , provided V' exists. If V is a vertex, the intervention of $M^{(1)}$ is unnecessary. $M^{(2)}$ is defined to be $M + SUV \cdot \overline{T}$ and V , being a vertex not contained in M , may be identified with β . The slight modifications required in the preceding process will easily be found.

The extension of Lemma 2 to the case where Σ is of order q is proved by exactly reversing the series of constructions used in proving Lemma 1. It is unnecessary to give the details.

Lemmas 1 and 2 are therefore proved.

If T is a vertex, γ , Lemma 1 has the following simpler form:

If S is any boundary component of an n -manifold, M , and γ a

vertex not belonging to M then $M \xrightarrow{12} M + S\Sigma\gamma$, where Σ is the shell of the S -cluster in \overline{M} .

This is the case of the lemma which will be used subsequently. The addition of the array $S\Sigma\gamma$ to M will be called "completing the S -cluster in M ."

Theorem 1. *If Δ and M are two similar bounded n -manifolds, then $\Delta \xrightarrow{12} M$.*

It is sufficient to shew that a substitution of type 3 can be effected by moves of types 1 and 2. Let the substitution of $T \cdot \overline{S}$ for $S \cdot \overline{T}$ in Δ be a move of type 3.

Suppose first that a boundary face, X , of $S \cdot \overline{T}$ belongs to $\overline{\Delta}$. If other boundary faces, Y, Z, \dots of $S \cdot \overline{T}$ belong to Δ let simplexes $\eta Y, \zeta Z, \dots$ be added to Δ , the vertices η, ζ , being different from each other and not contained in Δ . If Δ^* is the manifold obtained in this way, let the cluster in Δ^* at each internal component of the $(n-1)$ -element common to $S \cdot \overline{T}$ and $\Delta^* - S \cdot \overline{T}$ which is not also interior to Δ^* be completed by moves of types 1 and 2 (in each case with a different vertex). The array $S \cdot \overline{T}$ can now, by I 45 and I 38, be removed and replaced by its complement, $T \cdot \overline{S}$, by moves of types 1 and 2. If the added "constructional" clusters are removed, by reversing the sequence by which they were added, the required manifold $\Delta - \overline{S} \cdot T + \overline{T} \cdot S$ is obtained.

If $S \cdot \overline{T}$ has no face in $\overline{\Delta}$, Δ can be modified by moves of types 1 and 2 until it has. For the members of a chain (say (X_r)), connecting $S \cdot \overline{T}$ to a unit of Δ with a face in $\overline{\Delta}$ can be removed one by one, the cluster at the component of X_r opposite the free component being completed, if necessary, before X_r is removed. We can now replace $S \cdot \overline{T}$ by $T \cdot \overline{S}$, and retrace the steps by which the face of $S \cdot \overline{T}$ was freed, using only moves of types 1 and 2. The presence of the new component, T , does not interfere with the reversed series of "constructional" moves; for the removal of the added constructional clusters can certainly proceed as before (Lemma 2); and the presence of the internal component, T , could only interfere with the replacing of a unit of Δ itself if that unit contained T , which is excluded by the condition that the substitution of $T \cdot \overline{S}$ for $S \cdot \overline{T}$ is a regular move of type 3.

The theorem is therefore proved in all cases.

§ 2. Replacement of Moves of Types 1 and 2.

If U is a component, ($d(U) > 0$), of an n -array, Γ , the array is said to be subdivided through U , with vertex a , if every unit UX of Γ containing U is replaced by the array $a \cdot \overline{U} \cdot X$, formed by joining to a those faces of UX which do not contain U . The vertex a is the same for each simplex, and must not be contained in Γ .

Lemma 3. *If Γ and Δ are the arrays obtained by subdivision, through*

PR , with vertex a , of the primitive clusters $PQ.\overline{RS}$ and $RS.\overline{PQ}$ respectively, then

$$\Gamma \xrightarrow{3} \Delta, \quad [\mu | \text{not } aS, RS] \text{ } ^1).$$

(Any combination of P, Q, R , and S may be absent, provided the theorem remains significant).

Γ is $aQ.\overline{PR}.\overline{S} + PQS.\overline{R}$, which is $PQ.\overline{aS}.\overline{R} + aQR.\overline{P}.\overline{S}.$ Δ is, similarly, $RS.\overline{aQ}.\overline{P} + aSP.\overline{R}.\overline{Q}$.

Hence:

$$\begin{aligned} \Gamma &\xrightarrow{3} aS.\overline{PQ}.\overline{R} + aQR.\overline{P}.\overline{S}, & [\mu | \text{not } aS], & (\text{cf. I } 36), \\ &\text{is } aQ.\overline{RS}.\overline{P} + aPS.\overline{Q}.\overline{R}, \\ &\xrightarrow{3} RS.\overline{aQ}.\overline{P} + aPS.\overline{Q}.\overline{R}, & [\mu | \text{not } RS], \\ &\text{is } \Delta. \end{aligned}$$

When P and S are absent we have the better result:

$$Q.\overline{R} \xrightarrow{3} a.\overline{Q}.\overline{R}, \quad [\mu | \text{not } a],$$

and when Q and R are absent

$$a.\overline{P}.\overline{S} \xrightarrow{3} S.\overline{P}, \quad [\mu | \text{not } S].$$

These may be obtained either by noticing that only one of the two substitutions made in the general case is now necessary or directly from I 36.

Theorem 2. If Δ and M are two bounded n -manifolds, such that $\Delta \xrightarrow{3} M$, and if Γ is an n -array, containing no internal component of Δ or M , such that $\Gamma + \Delta$ is a manifold, then $\Gamma + \Delta \xrightarrow{3} \Gamma + M$.

An attempt to transform $\Gamma + \Delta$ into $\Gamma + M$ by the given series of moves which changes Δ into M may fail. For although no internal component of either Δ or M belongs to Γ , it may happen that a component of Γ is introduced in the process ($\Delta \rightarrow M$), to disappear again subsequently. The process must therefore be modified.

Consider first the case in which only one such interference occurs. Suppose that the process ($\Delta \rightarrow M$) includes the move $(U.\overline{V} \rightarrow V.\overline{U})$, where V is a component of Γ . Let the series of moves which precedes $(U.\overline{V} \rightarrow V.\overline{U})$ in the original ($\Delta \rightarrow M$) series be applied to $\Gamma + \Delta$, and then let $\overline{U}.V$ be changed, not to $V.\overline{U}$, but (Lemma 3) to $a.\overline{U}.V$, a being "new". If the moves ($\Delta \rightarrow M$) are now again carried on, a substitution of the form $(PQ.\overline{RS} \rightarrow \overline{RS}.PQ)$ will eventually present itself, where PR is V . In the array, Γ^* , which has at this point been derived from $\Delta + I$,

¹⁾ This symbol has the meaning of the similar symbol defined on p. 622, with the added condition that Φ is such that $\Phi + \Gamma$ is a manifold. The use of the symbols $[\text{not } PQ, \dots | \mu]$ and $[\mu | \mu]$ is also contemplated. If it is known that $\Gamma \xrightarrow{pq} \Delta$, $[\text{not } PQ]$, and P is interior to Γ it may be inferred that $\Gamma \xrightarrow{pq} \Delta$, $[\mu | \text{not } Q]$. For if $\Phi + \Gamma$ is a manifold, (Φ and Γ having no common unit), P cannot belong to Φ .

The symbol $\Phi \xrightarrow{pq} \Psi$ without an added condition of course retains its original meaning that Φ , (alone), can be transformed into Ψ , (alone), by moves of types p and q .

the place of $PQ.\overline{RS}$ is taken by the array formed by subdividing it through PR with vertex α . The original move substituting $\overline{RS}.PQ$ for $PQ.\overline{RS}$ must therefore be replaced by a series of moves which substitutes the one cluster, subdivided through PR , for the other, also subdivided through PR . By Lemma 3 this series of moves exists. For if αS belongs to Γ^* it must have been introduced by the substitution $(U.\overline{V} \rightarrow \alpha.\overline{U}.\overline{V})$, and is therefore a component of $\alpha.\overline{U}.\overline{V}$. Since V is PR , this implies that S is a component of \overline{U} and RS a component of $\alpha.\overline{U}.\overline{V}$. Now just as α , the vertex of subdivision of PR , remains in the new series no longer than PR in the old, so αS remains no longer than PRS , and certainly no longer than RS . But, from the hypothesis that there is only one interference, it follows that RS , and therefore also αS , does not belong to Γ^* . The substitution can therefore be effected.

It is now obvious that the $(\Delta \rightarrow M)$ process can be followed to the end. If the set finally reached is $\Gamma + M^*$, the only possible difference between M and M^* is that the V -cluster in M should appear subdivided through V in M^* . But V belongs to Γ and is therefore not a component of M . It must have disappeared in the course of $(\Delta \rightarrow M)$, and $\alpha.\overline{V}$ disappeared at the corresponding stage of the modified series. M and M^* are therefore identical.

In the general case let the intrusive components of Γ be arranged in order, say as U^1, U^2, \dots, U^i being the last to intrude, U^2 the next but last, and so on. Let successive processes for transforming Δ into M be constructed, the first by modifying the original series of moves, $(\Delta \rightarrow M)$, so that the interference with U^1 is avoided; the second by modifying this new series so that U^2 does not interfere; and so on. From the nature of the modifications none of the components (U^i) need ever be re-introduced. The sequence of moves finally obtained therefore gives a method for transforming $\Gamma + \Delta$ into $\Gamma + M$.

Theorem 3a. *If Δ and M are similar bounded n -manifolds, $\Delta \xrightarrow{13} M$.*

This theorem is clearly true if $n=1$. Suppose it true if $n \leq m-1$. We first deduce the following lemma from this assumption.

Lemma 4. *($n \leq m$). If E is an $(n-1)$ -element, and α and β vertices not belonging to it, $\alpha E \xrightarrow{3} \beta.\overline{\alpha E}$, $[\mu \mid \text{not } \beta]$.*

By the inductive hypothesis either (a) E is $E^* + ST$, (S internal and T free), or (b) E is $E^* - V.\overline{U} + U.\overline{V}$, where E^* is an $(n-1)$ -element of lower order¹⁾, (1,3) than E . We may assume that $\alpha E^* \xrightarrow{3} \beta.\overline{\alpha E^*}$, $[\mu \mid \text{not } \beta]$.

(a). Let \overline{E} be $\Gamma + T.\overline{S}$, so that E^* is $\Gamma + S.\overline{T}$.

$$\alpha E \xrightarrow{3} \beta.\overline{\alpha E^*} + \alpha ST, \quad [\mu \mid \text{not } \beta], \quad (\text{by Theorem 2}),$$

$$\text{is } \beta(\alpha\Gamma + E^*) + \alpha S.\overline{\beta T},$$

$$\xrightarrow{3} \beta(\alpha\Gamma + E^*) + \beta T.\overline{\alpha S}, \quad \text{which is } \beta.\overline{\alpha E}.$$

¹⁾ E is of order q , (r, s) if it can be obtained from a simplex by q moves of types r and s .

$$\begin{aligned}
 (b). \quad aE \xrightarrow{3} \beta \cdot \overline{aE^*} - aV \cdot \overline{U} + V \cdot \overline{aU}, \text{ is } \beta \cdot \overline{aE^*} + UV, \\
 \text{is } \beta(E - U \cdot \overline{V}) + V \cdot \overline{\beta U} + \beta a \cdot \overline{E}, \text{ (since } \overline{E^*} \text{ is } \overline{E}), \\
 \xrightarrow{3} \beta(E + a \cdot \overline{E}).
 \end{aligned}$$

Proof of Theorem 3a. It must be shewn that a move of type 2, applied to an m -dimensional manifold, can be replaced by a series of moves of types 1 and 3.

Let the move be the removal of ST from Δ , S being interior to Δ and T free. Let a be a vertex of S , and suppose first that S has other vertices: say, S is aS' . The S -cluster in Δ may be regarded as an incomplete star with core a , and may, (Lemma 4), be transformed into a complete star, $\gamma \cdot \overline{S\Sigma}$ with a new core, γ . The component S is thus eliminated from Δ , and the new manifold, Δ^* , has regular contact with ST .

In the manifold $\Delta^* + ST$ the units containing vertices of S form the array $\gamma\Sigma \cdot \overline{S} + ST$ or, (setting Δ for $\Sigma - T$), $\gamma\Delta \cdot \overline{S} + T \cdot \overline{\gamma S}$. Hence $\Delta^* + ST$ is $(\Delta - S\Sigma) + \gamma\Delta \cdot \overline{S} + \overline{\gamma S} \cdot T$, and

$$\Delta^* + ST \xrightarrow{3} (\Delta - S\Sigma) + \gamma(\Delta \cdot \overline{S} + S \cdot \overline{T}).$$

The part of the sphere $\Delta \cdot \overline{S} + S \cdot \overline{T}$ not containing a is $\Delta S'$. Hence it follows, by reversing the process of Lemma 4, that

$$\Delta^* + ST \xrightarrow{3} \Delta - S\Sigma + a \cdot \Delta S';$$

for $\Delta - S\Sigma$ does not contain S . Since $\Sigma - \Delta$ is T and aS' is S the theorem is proved unless S is a vertex.

If S is a the substitutions used are

$$[\Delta - a\Sigma +] a\Sigma \xrightarrow{3} \gamma\Sigma \xrightarrow{1} \gamma\Sigma + aT, \text{ is } T \cdot \overline{a\gamma} + \gamma\Delta, \xrightarrow{3} a\gamma \cdot \overline{T} + \gamma\Delta \xrightarrow{3} a\Delta$$

the addition of $\Delta - a\Sigma$ being understood at each stage.

Theorem 3b. If Δ and M are equivalent bounded n -manifolds, $\Delta \xrightarrow{23} M$. (For if $\Delta \rightarrow M$, $M \rightarrow \Delta$).

Theorem 4. If E^1 and E^2 are two n -elements with the same boundary, $E^1 \xrightarrow{3} E^2$.

It is sufficient to shew that $E^1 \xrightarrow{3} a \cdot \overline{E^1}$, where a is a vertex not belonging to E^1 .

Suppose this true when the element is of order less than q , (1,3). Let E^1 be $E^* + ST$, where E^* is of order $(q-1)$, (1,3), S is interior to E^1 , and T is free. Let Γ be $\overline{E^1} - T \cdot \overline{S}$, so that $\overline{E^*}$ is $\Gamma + S \cdot \overline{T}$.

$$\begin{aligned}
 a\overline{E^1} \text{ is } a(\Gamma + T \cdot \overline{S}), \\
 \xrightarrow{3} a\Gamma + S \cdot \overline{aT}, \\
 \text{is } a \cdot \overline{E^*} + ST, \\
 \xrightarrow{3} E^* + ST, \text{ (which is } E^1),
 \end{aligned}$$

provided the presence of ST does not interfere with the last step. This condition is clearly fulfilled, in virtue of Theorem 2, since the contact of ST with E^* is regular.

Theorem 5. *If Λ and M are equivalent unbounded n -manifolds, then $\Lambda \xrightarrow{3} M$.*

Let S and T be units of Λ and M respectively, such that $\Lambda - S$ can be transformed into $M - T$ by q moves of types 2 and 3. Let the manifold obtained after j moves be Θ_j , so that $\Lambda - S$ is Θ_0 , and $M - T$ is Θ_q . Let Λ_0 be Λ and suppose there is an unbounded manifold, Λ_j , containing Θ_j , such that $\Lambda \xrightarrow{3} \Lambda_j$ and $\Lambda_j - \Theta_j$ is an n -element. If $\Theta_j \xrightarrow{2} \Theta_{j+1}$ let Λ_{j+1} be Λ_j ; if the move changing Θ_j into Θ_{j+1} is the substitution of $V \cdot \bar{U}$ for $U \cdot \bar{V}$ let Λ_{j+1} be obtained from Λ_j by moves of type 3 by first, (if necessary) eliminating V from $\Lambda_j - \Theta_j$ (using the method of Theorem 3a), and then making the (now regular) move: $U \cdot \bar{V} \rightarrow V \cdot \bar{U}$. The manifold Λ_{j+1} bears the same relations to $j+1$ as Λ_j to j . Hence Λ_j exists if $0 \leq j \leq q$. Λ_q is an unbounded n -manifold containing $M - T$, and $\Lambda_q - (M - T)$ is an n -element whose boundary is \bar{T} . The transformation of Λ into M by moves of type 3 is therefore completed by changing $\Lambda_q - (M - T)$ into T .

II. Manifolds as Sums of Elements.

§ 3. Combinations of Elements and Manifolds.

Theorem 6. *If in an n -manifold, M , an array of simplexes forming an n -element, E^1 , is replaced by an n -element, E^2 , whose boundary is identical with \bar{E}^1 , but of which no internal component belongs to $M - E^1$, the result is a manifold equivalent to M .*

(This follows immediately from Theorems 4 and 2, and, (if M is unbounded), I 21. Clearly, if M is unbounded, $M \xrightarrow{3} M - E^1 + E^2$.)

Corollary 1. *If E_n^1 and E_n^2 have identical boundaries, but no other common components or units, $E_n^1 + E_n^2$ is an n -sphere.*

By Theorem 6, $E_n^1 + E_n^2 \rightarrow E_n^1 + a \cdot \bar{E}_n^2$, which is $a \bar{E}_n^1$, a sphere.

Corollary 2. $\Sigma_n - E_n$ is an n -element.

For $\Sigma_n - E_n + a \cdot \bar{E}_n$ is an n -sphere, and therefore $\Sigma_n - E_n$ is an n -element. (Cf. the proof of I 28).

Lemma 5a. *If E is drawn on M and a is a vertex not belonging to M , then $M \rightarrow M + aE$.*

Let the lemma be assumed true for elements of lower order, (1,3), than E .

If E is obtainable from E^* , of lower order (1,3), by the regular addition of S , $M \rightarrow M + aE^*$ and aS has regular contact with $M + aE^*$.

If E is obtainable from E^* by the regular substitution of $U \cdot \bar{V}$ for $V \cdot \bar{U}$ we first modify M so that it does not contain V , using the process of Theorem 3, preceded, if necessary, by the completion of the V -cluster. Since V does not belong to E , the boundary of the new manifold, M^* , still contains E , and UV has regular contact with M^* . In $\overline{M^* + UV}$, E is replaced by E^* and therefore $M^* + UV \rightarrow M^* + UV + aE^*$. This manifold is easily transformed into $M^* + aE$, and thence into $M + aE$.

Lemma 5b. If aE is the a -star in M , and no internal component of E belongs to \bar{M} , then $M \rightarrow M - aE$:

(cf. Lemma 5a).

Theorem 7. Let M be a bounded n -manifold, E an n -element contained in it, and suppose that there is an $(n-1)$ -element, E^* , contained in \bar{E} , such that all common components of E and $M - E$ belong to E^* . Let E' be a second n -element whose boundary contains E^* , but which contains no other component of $M - E$. Then $M \rightarrow M - E + E'$.

If \bar{E} is $E^* + e$ and \bar{E}' is $E^* + e'$, and if a is a new vertex, $E + ae$ and $E' + ae'$ are two n -elements with the same boundary, viz. $E^* + a \cdot \bar{E}^*$.

Hence:

$$M \xrightarrow{12} M - E + E + ae \quad (\text{Lemma 5a}),$$

$$\xrightarrow{3} M - E + E' + ae'. \quad (\text{Theorem 4}),$$

$$\xrightarrow{12} M - E + E' \quad (\text{Lemma 5b}).$$

In the circumstances of Theorem 7 E and E' will be said to have similar contact with $M - E$.

Lemma 6. If $a\Sigma$ is drawn on \bar{M} , and if \bar{E} is Σ , while E has no further components in M , then $M \rightarrow M + aE$.

If E is itself a complete star the lemma is reduced to a case of Lemma 5a. Suppose then, that the truth of the theorem is known for elements which can be transformed into complete stars in a smaller number of moves of type 3. If E is obtained from E^* , of lower order (in this sense), by the regular substitution of $U \cdot \bar{V}$ for $V \cdot \bar{U}$, V does not belong to E , nor, therefore, to Σ nor to $a\Sigma$. If it belongs to M let it be eliminated. (cf. Lemma 5a). The manifold, M^* , so obtained still contains $a\Sigma$ in its boundary, but contains no internal component of E^* . Hence $M^* \rightarrow M^* + aE^*$, which is easily transformed $M + aE$.

Theorem 8a. If the common part of M_n and E_n is an $(n-1)$ -element lying in the boundary of each, then $M_n \rightarrow M_n + E_n$.

Let γ be a vertex not belonging to M_n or E_n and let E^1, E^2 be the parts of E_n which respectively do and do not belong to M_n .

$$M_n \rightarrow M_n + \gamma E^1, \quad (\text{Lemma 5a})$$

$$\rightarrow M_n + \gamma (E^1 + E^2), \quad (\text{Lemma 6})$$

$$\rightarrow M_n + E_n \quad (\text{Theorems 4 and 2}).$$

Corollary to Theorem 8a. *The sum of two n -elements whose common components form a boundary $(n-1)$ -element of each is an n -element.*

Lemma 7a. *If E is an element and Π a sphere or element having no vertex in common with E , $E\Pi$ is an element.*

Lemma 7b. *If Σ and Σ' have no common vertex, $\Sigma\Sigma'$ is a sphere.*

(By using the corollary to Theorem 8a, Lemma 7a can be deduced from the case when E is a simplex; and Lemma 7b can then be proved by considering $(\Sigma-S)\Sigma' + S\Sigma'$, where S is a unit of Σ).

Theorem 9a. *If the common components of two bounded n -manifolds form a number of $(n-1)$ -manifolds lying in the boundary of each, no two of them having a common vertex, the sum of the two n -manifolds is an n -manifold.*

(The corollaries to Theorems 6 and 8a shew that the units of both manifolds at a common vertex form an n -star, complete if the vertex is interior to a common $(n-1)$ -manifold, incomplete if it is not).

Theorem 8b. *If M_n contains E_n , and the part of E_n in $\overline{M_n}$ is an $(n-1)$ -element, then $M_n \rightarrow M_n - E_n$.*

(Cf. Theorem 8a.)

Theorem 9b. *If M_n^2 is drawn on M_n^1 and the components (if any) of M_n^2 in the boundary of M_n^1 form a number of $(n-1)$ -manifolds, no two of them having a common vertex, then $M_n^2 - M_n^1$ is a bounded n -manifold.*

(Cf. Theorem 9a.)

§ 9. Normal sets of cells.

Let \mathcal{E} be a set of elements, (the "cells of \mathcal{E} "), of all dimension numbers from 0 to n , such that:

(Ni) every cell of less than n dimensions is contained in another cell;

(Nii) two cells have in common either nothing or a cell of lower dimension number than at least one of them;

(Niii) no internal component of a cell belongs to a cell of lower dimension number;

(Niv) the boundary of the n -cells is made up of $(n-1)$ -cells;

then \mathcal{E} is said to be a *normal n -set of cells*. The n -array which is the sum of the n -cells of \mathcal{E} may without confusion be called "the n -array \mathcal{E} ".

Clearly two k -cells cannot have a common unit; and if a unit or internal component of a j -cell belongs to a k -cell ($j \leq k$) the j -cell is contained in the k -cell. If a unit or internal component of a cell belongs to $\overline{\mathcal{E}}$ the whole of the cell belongs to $\overline{\mathcal{E}}$.

Lemma 8a. *Every k -cell of \mathcal{E} is contained in a $(k+1)$ -cell of \mathcal{E} .*

Lemma 8b. *The boundary of a $(k+1)$ -cell is a sum of k -cells.*

$$(0 \leq k \leq n-1).$$

Both lemmas being true when $k=n-1$, suppose them true when $k \geq j$. Every $(j-1)$ -cell, G_{j-1} , is contained in the boundary of an r -cell, where $r \geq j$. If $r > j$ \overline{G}_r is, by the hypothesis concerning Lemma 8b, a sum of $(r-1)$ -cells, and therefore G_{j-1} belongs to an $(r-1)$ -cell. Repetition of this argument finally shews that G_{j-1} belongs to a j -cell, say G_j . G_j itself belongs to the boundary of a $(j+1)$ -cell, G_{j+1} ; and since \overline{G}_{j+1} is an unbounded manifold, every unit of \overline{G}_j is common to G_j and at least one other j -cell, and therefore, by Nii, belongs to a $(j-1)$ -cell. The lemmas are therefore proved.

From Lemma 8a it follows that any subset of the k -cells of \mathcal{E} , together with all the cells contained in them, form a normal k -set.

Let \mathcal{E} and \mathcal{E}' be two normal n -sets of cells, and suppose a (1,1) correspondence can be set up between the cells of \mathcal{E} and those of \mathcal{E}' so that correlated cells have the same dimension number, and the correlate of the common part of two cells of \mathcal{E} is the common part of their correlates in \mathcal{E}' , and *vice versa*. Then \mathcal{E} and \mathcal{E}' are said to have the *same structure*.

The sum of the n -cells of a normal n -set, \mathcal{E} , which contain a given k -cell, G_k , will be denoted by $G_k \mathcal{E}$.

Theorem 10. *If \mathcal{E} and \mathcal{E}' are normal n -sets with the same structure, and the n -array \mathcal{E} is an n -manifold, the n -array \mathcal{E}' is a topologically equivalent n -manifold.*

First part of the proof. It will first be shewn that the n -array \mathcal{E} is equivalent to the sum of the n -cells of a normal n -set with the same structure as \mathcal{E} , but of which all the cells are complete stars.

Any $(n-1)$ -cell, G_{n-1} , of \mathcal{E} either belongs to $\overline{\mathcal{E}}$ or lies in the boundaries of two n -cells, of which it is the common part. In any case $G_{n-1} \mathcal{E}$ is an n -element. Let it be assumed that $G_r \mathcal{E}$ is an n -element when $r > k$; and also that if Z is a normal m -set and G_p any of its cells, $G_p Z$ is an m -element if $m < n$.

Let G_p be a cell of Ξ , G_q a cell contained in G_p but not identical with it. By the inductive hypothesis $G_q \overline{G_p}^{(1)}$ is a $(p-1)$ -element, and so, therefore, is the remainder of $\overline{G_p}$, which will be written $-_{G_q} \overline{G_p}$. Clearly if G_p is interior to the n -array Ξ , and $G_n^{(i)}$, ($i=1, 2, \dots$), are the n -cells containing it then $B(G_p \Xi)$ is $\sum_i -_{G_p} \overline{G_n^{(i)}}$.

If G_p contains G_q , and G_q contains (but is not) G_r , $-_{G_r} \overline{G_q}$ is the part of G_q contained in $-_{G_r} \overline{G_p}$. To prove this it is sufficient to consider the case $q=p-1$. G_{p-1} is then one of the $(p-1)$ -cells of $_{G_r} \overline{G_p}$ which is by hypothesis a $(p-1)$ -element to which G_r is interior. Hence $-_{G_r} \overline{G_{p-1}}$ is the contribution of G_{p-1} to $B(_{G_r} \overline{G_p})$. But $B(_{G_r} \overline{G_p})$ is $B(-_{G_r} \overline{G_p})$, and therefore $-_{G_r} \overline{G_{p-1}}$ belongs to $-_{G_r} \overline{G_p}$.

If G_p and G_q have G_s in common, and G_r is contained in G_s , the common part of $-_{G_r} \overline{G_p}$ and $-_{G_r} \overline{G_q}$ is $-_{G_r} \overline{G_s}$. For by the result just obtained, $-_{G_r} \overline{G_s}$ belongs to both $-_{G_r} \overline{G_p}$ and $-_{G_r} \overline{G_q}$; and since no internal component of $_{G_r} \overline{G_s}$ belongs to either $-_{G_r} \overline{G_p}$ or $-_{G_r} \overline{G_q}$, the common part is precisely $-_{G_r} \overline{G_s}$.

The first part of the main theorem can now be proved. Let G_{k+1} be a $(k+1)$ -cell of Ξ , α a new vertex, Ξ^* the set of elements obtained from Ξ by replacing G_{k+1} by $\alpha \cdot \overline{G_{k+1}}$ and each cell, G_p , containing G_{k+1} by $\alpha \cdot -_{G_{k+1}} \overline{G_p}$, leaving the rest unaltered. From the two results just established it is clear that Ξ^* is a normal n -set having the same structure as Ξ , and that if the n -cells of Ξ containing G_{k+1} are $G_n^{(i)}$, ($i=1, 2, \dots$), the new n -cells form the array $\alpha \cdot \sum_i -_{G_{k+1}} \overline{G_n^{(i)}}$, say Θ . If G_{k+1} is interior to the n -array Ξ , Θ is $\alpha \cdot B(G_{k+1} \Xi)$ and $B(\Theta)$ is $B(G_{k+1} \Xi)$. If G_{k+1} belongs to Ξ , $_{G_{k+1}} \Xi$ is (by the inductive hypothesis) an $(n-1)$ -element, E_{n-1} , and $B(G_{k+1} \Xi)$ is $\sum_i -_{G_{k+1}} \overline{G_n^{(i)}} + E_{n-1}$, while $B(\Theta)$ is $\sum_i -_{G_{k+1}} \overline{G_n^{(i)}} + \alpha \cdot \overline{E_{n-1}}$, $\alpha \cdot \overline{E_{n-1}}$ lying in $B(\Xi^*)$. Hence in either case $\Xi^* \rightarrow \Xi$ ³⁾ (cf. Theorems 6 and 7). Now let the group of cells containing a $(k+1)$ -cell of Ξ^* , (other than $\alpha \cdot \overline{G_{k+1}}$), be similarly treated; and let this process be continued until first all the $(k+1)$ -cells, then the $(k+2)$ -, $(k+3)$ -, ... and finally the n -cells of Ξ have been replaced. It will easily be verified that the set of elements, $\Xi^{(k)}$, finally obtained has the following properties:

1) $_{G_q} \overline{G_p}$ means $_{G_q} (\overline{G_p})$, not $(\overline{_{G_q} G_p})$.

2) $B(\Gamma)$ will be written for "the boundary of Γ " when $\overline{\Gamma}$ is not convenient.

3) The use of the sign " \rightarrow " implies, of course, that the n -arrays Ξ , Ξ^* are referred to.

- (1) $\Xi^{(k)}$ is a normal n -set with the same structure as Ξ ;
- (2) $\Xi^{(k)} \rightarrow \Xi$;
- (3) every j -cell of $\Xi^{(k)}$ for which $j > k$ is a complete j -star;
- (4) the j -cells of $\Xi^{(k)}$ for which $j \leq k$ are identical with those of Ξ ;
- (5) if G_j is a j -cell of $\Xi^{(k)}$ (where $j > k$) $G_j \Xi^{(k)}$ is an n -element;
- (6) if G_j is a j -cell of Ξ (where $j \leq k$), $G_j \Xi^{(k)} \rightarrow_{G_j} \Xi$, provided one of the two is known to be a manifold.

This has been proved from the initial assumption that when $0 \leq r < k$ $G_r \Xi$ is an n -element. If then it can be shewn that this assumption is true when $0 \leq r < n$ the first part of the proof is completed; and for this it is sufficient to extend the range by 1, and also, (by (6)) to consider $\Xi^{(k)}$ instead of Ξ ; i.e. we have to shew that if G_k is a k -cell of $\Xi^{(k)}$, $G_k \Xi^{(k)}$ is an n -element.

Now if G_r is any r -cell of $\Xi^{(k)}$, ($r \geq k$), the sum of all units of $\Xi^{(k)}$ containing a unit of G_r has the form $G_r \Pi_{n-r-1}$, where Π_{n-r-1} is an $(n-r-1)$ -sphere or an $(n-r-1)$ -element. For suppose this statement true of normal sets of the type of $\Xi^{(k)}$ but of lower dimension number.¹⁾ Since $\Xi^{(k)}$ is known to be a manifold, it is only necessary to shew that, if S_r and S'_r are units of G_r , the shells of the S_r - and S'_r -clusters in $\Xi^{(k)}$ are identical. Let $\alpha \Sigma_{n-1}$ be an n -cell containing G_r . Σ_{n-1} is a normal $(n-1)$ -set of the type of $\Xi^{(k)}$ and therefore those of its units which contain a unit of G_r form an array $G_r \Pi_{n-r-2}$. Hence the units of $\alpha \Sigma_{n-1}$ containing a unit of G_r form the array $G_r \alpha \Pi_{n-r-2}$; and therefore if $S_r T_{n-r-1}$ belongs to $\alpha \Sigma_{n-1}$ so does $S'_r T_{n-r-1}$.

Suppose then that G_n is an n -cell of $\Xi^{(k)}$ containing a given k -cell G_k , and let α be the centre of G_n . The element $\alpha \cdot_{-G_k} \overline{G_n}$ has the $(n-1)$ -element $\alpha \cdot B (-_{G_k} \overline{G_n})$ and nothing more in common with the rest of $G_k \Xi^{(k)}$, and can therefore be removed from it by moves of types 1 and 2, provided the remainder can be shewn to be a manifold. Moreover every internal component of $\alpha \cdot B (-_{G_k} \overline{G_n})$ contains α , a vertex belonging to no other n -cell. Hence the analogous groups corresponding to all n -cells containing G_k can be removed, in any order, by moves 1 and 2 provided Δ^{k+1} , the remainder, is an n -manifold. Let G_{n-1} be an $(n-1)$ -cell of $\Xi^{(k)}$ containing G_k , let β be its centre and $\Pi_0 G_{n-1}$ the set of units of $\Xi^{(k)}$ at G_{n-1} . The array $\beta \Pi_0 \cdot_{-G_k} \overline{G_{n-1}}$ is contained in Δ^{k+1} and has in common with the rest of it the element $\beta \Pi_0 B (-_{G_k} \overline{G_{n-1}})$; for of the units of $\Xi^{(k)}$ containing $\Pi_0 \cdot_{-G_k} \overline{G_{n-1}}$ those not belonging to $\Pi_0 G_{n-1}$ do not belong to Δ^{k+1} . Hence if the removal from Δ^{k+1} of $\beta \Pi_0 \cdot_{-G_k} \overline{G_{n-1}}$ and the analogous arrays corresponding to other $(n-1)$ -cells containing G_k leaves the n -array Δ^{k+2} , $\Delta^{k+1} \rightarrow \Delta^{k+2}$, provided either is a manifold. The further progress of this dismantling process is now obvious. If G_r is an r -cell of $\Xi^{(k)}$ containing G_k , α its centre and $\Pi_{n-r-1} G_r$

¹⁾ i.e. sets of lower dimension number bearing the same relations ((3) and (5) above) to some number i as $\Xi^{(k)}$ does to k .

the array of units of $\Xi^{(k)}$ containing it, Δ^{k+n-r} contains $\kappa \Pi_{n-r-1} \cdot \dots_{G_k} \overline{G_r}$, which has in common with the rest of Δ^{k+n-r} the $(n-1)$ -element $\kappa \Pi_{n-r-1} B(-_{G_k} \overline{G_r})$. The removal of this and the other analogous arrays from Δ^{k+n-r} leaves an array, $\Delta^{k+n-r+1}$, which contains those units, and those only, of $\Xi^{(k)}$ which have as component a unit of some $(r-1)$ -cell containing G_k ; and $\Delta^{k+n-r+1} \xrightarrow{12} \Delta^{k+n-r}$ provided either is a manifold. Finally, then, we obtain an n -array, Δ^n , containing those units of $_{G_k} \Xi^{(k)}$ which have as a component some unit of G_k itself; and $\Delta^n \rightarrow _{G_k} \Xi^{(k)}$ provided Δ^n is a manifold. But Δ^n is $G_k \Pi_{n-k-1}$, an n -element; and $_{G_k} \Xi^{(k)}$ is therefore also an n -element. This completes the first part of the proof.

Second part of the proof. It remains to shew that if Ξ^0 is a normal set, all of whose cells are complete stars, and the n -array Ξ^0 is a manifold, and if Ξ' is a normal n -set with the same structure as Ξ^0 , then $\Xi^0 \rightarrow \Xi'$. This cannot be proved by a mere reversal of the preceding argument since it is now Ξ^0 , not Ξ' , which is known to be an n -manifold.

It has been shewn that if G_1 is a 1-cell of Ξ^0 , and an r -cell, G_r , contains the unit SX , where S is a unit of G_1 , then G_r contains the array $G_1 X$: and no vertex of X belongs to a 1-cell of Ξ^0 . Let every such array, $G_1 X$, in every cell of Ξ^0 be replaced by $H_1 X$, where H_1 is a 1-element congruent to the image of G_1 in Ξ' ,¹⁾ but such that $\overline{H_1}$ is $\overline{G_1}$, and all internal vertices of H_1 are new. The effect of one such substitution on any cell, G_r , of Ξ^0 is that an r -element $G_1 E_{r-2}$, contained in G_r , is replaced by $H_1 E_{r-2}$, having similar contact²⁾ with the rest of G_r ; and the effect on the n -array Ξ^0 is that an element $G_1 \Pi_{n-2}$ is replaced by an element $H_1 \Pi_{n-2}$, having similar contact with the rest of Ξ^0 . Moreover, owing to the fact that E_{r-2} and Π_{n-2} respectively contain no vertex of any 1-cell of Ξ^0 , these statements remain true if any number of these substitutions corresponding to other cells have already taken place³⁾. Hence the effect of all the substitutions is to give a normal n -set of cells, Γ^1 , having the same structure as, and equivalent to, Ξ^0 . The 1-cells of Γ^1 are congruent to those of Ξ' ; its

¹⁾ i.e. the cell in Ξ' correlated to G_1 in Ξ^0 .

²⁾ Cf. p. 635.

³⁾ It is perhaps not obvious that, (e.g.), if a number of other substitutions, leading say to the array Θ , have preceded the substitution of H_1 for G_1 , then all common components of $H_1 \Pi_{n-2}$ and the rest of Θ belong to $\overline{H_1} \Pi_{n-2}$ (part of the conditions for regular contact). All the components of $H_1 \Pi_{n-2}$ not in Π_{n-2} , $\overline{H_1}$ contain an internal component of H_1 . Since all the cells of Ξ^0 are complete stars, while internal vertices of H_1 are new, every component of Ξ^0 not in $\overline{H_1}$ contains a vertex not in H_1 . The only possible "interferences", then, are with the new cells of Θ_1 , congruent to cells of Ξ' . But any such interferences would imply corresponding ones in the normal set Ξ' itself; i.e. that an internal component of a 1-cell in Ξ' belongs to another cell of Ξ' of the same or lower dimensions, contrary to $N(ii)$ and $N(iii)$.

remaining cells are complete stars; and, if $r \geq 2$, the units of Γ^1 containing a unit of a cell G_r form an array $G_r \Pi_{n-r-1}$.

The boundaries of the 2-cells in Γ^1 are congruent to their correlates in Ξ' . It is therefore possible to substitute for all the arrays $G_2 X$ contained in cells of Γ^1 arrays $H_2 X$, where H_2 is a 2-element congruent to the image of G_2 in Γ^1 , but such that $\overline{H_2}$ is $\overline{G_2}$, and all internal components of H_2 are new; and the result is a normal n -set Γ^2 , having the same structure as and equivalent to Ξ^0 , whose 1- and 2-cells are congruent to those of Ξ' , while the remainder are complete stars. It is now clear that the process can be continued until finally a normal n -set congruent to Ξ' and equivalent to Ξ^0 is obtained. The proof of Theorem 10 is therefore completed.

In the course of proving Theorem 10 the following result has been established:

Theorem 11. *If the sum of the n -cells of a normal n -set, Ξ , is an n -manifold, the sum of the n -cells containing any k -cell of Ξ is an n -element ($0 \leq k \leq n-1$).*

Anatomy. — "*The ontogenetic development of the Claustrum in Mammals.*" By J. FAUL. (Communicated by C. U. ARIËNS KAPPERS.)

(Communicated at the meeting of March 27, 1926).

I have examined several embryonic specimens representing different orders of mammals in regard to the formations of the ventro-lateral sector of the brain-wall but in particular to the region of the pallio-striatal angle (pal. str. ang. fig. 1—4) in order to study the development of the claustrum.

Owing to the great similarity in the conformation of the parts in this region in nearly all the specimens an individual description is unnecessary. Only a general description will be given, reference being made to typical stages of different animals for the illucidation of my thesis.

When a section is examined from the middle of the hemisphere of a young mammalian embryo, we find the striatum to occupy a considerable extent of the lateral wall.

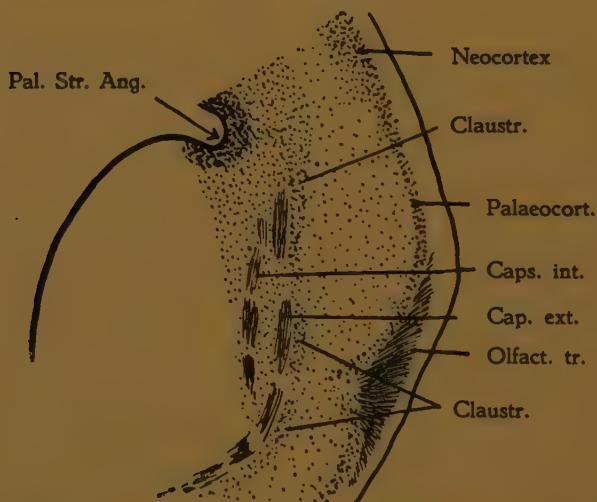


Fig. 1. Transverse section of an 11 mm. embryo of *Didelphys*.

Lateral or ventro-lateral to it will be seen a column at the pallio-striatal angle near the first capsular fibres. These cells (fig. 1) which represent the claustrum are similar in size and staining reaction to those of the perpendymal matrix with which they are continuous dorsally. In many cases the claustral cells are directed with their longest axis downwards and outwards, as noted by E. DE VRIES, who laid down that the direction of growth

of these cells is indicated by the direction of their greatest diameter (c.f. also HIS). Hence we may conclude that the growth of the claustrum takes place downwards and outwards, which is an important fact in my opinion, pointing to stimulative influences that may cause the claustrum to develop.

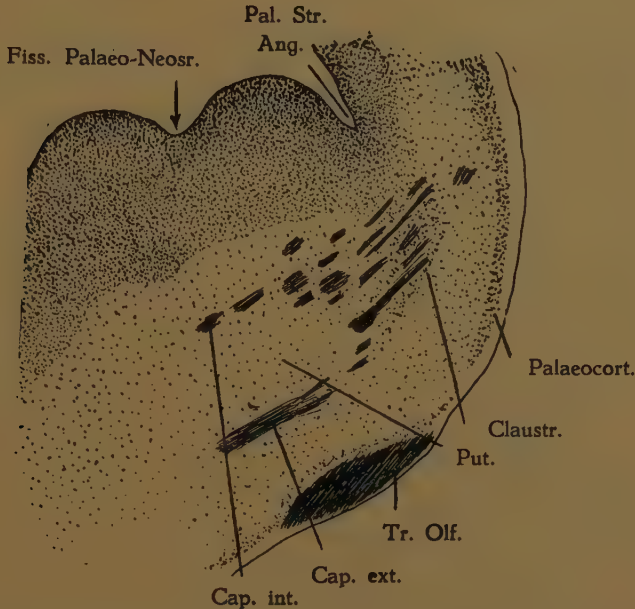


Fig. 2. Transverse section of a 30 mm. embryo of *Sus scropha*.

Reviewing a series of sections in an antero-posterior direction, we find that the claustrum lies adjacent to a fibre bundle (fig. 1 and 2). When the latter is followed posteriorly it is found to split into two parts, an upper and a lower, by the appearance between them of the anterior lateral end of the neostriatum, the putamen. The mesial fibres represent the upper part of the internal capsule, the lateral probably represent the external capsule and the ansa lenticularis, the latter being continuous laterally with the external capsule which turns up almost perpendicularly to separate the claustrum from the lentiform nucleus (fig. 3 and 4).

Above the pallio-striatal angle, along and above the line of entrance of the internal capsule into the cortex, the layers of the neopallium are developing by a periferal migration of cells from the ventricular matrix.

The upper end of the claustrum is in connection with the ventricular matrix where this joins the striatal matrix through the conjoined fibres of the internal and external capsules (fig. 2—4).

In some of the specimens, as for example *Sus Scropha* (fig. 2, 3) and *Bos taurus* the most ventral forebrain fibres are placed anteriorly rather laterally, much in the position of the external capsule. Lateral to them lies the ribbon-like claustrum in continuity above with the ventricular matrix

between the uppermost fibres of the external and internal capsules. The fibres are very abundant and seem to congregate especially at this point.

A consideration of my embryos shows that in every case the claustrum is attached to the ventricular matrix where the latter adjoins the striatal matrix, the claustral cells passing between the capsular fibres, the origin

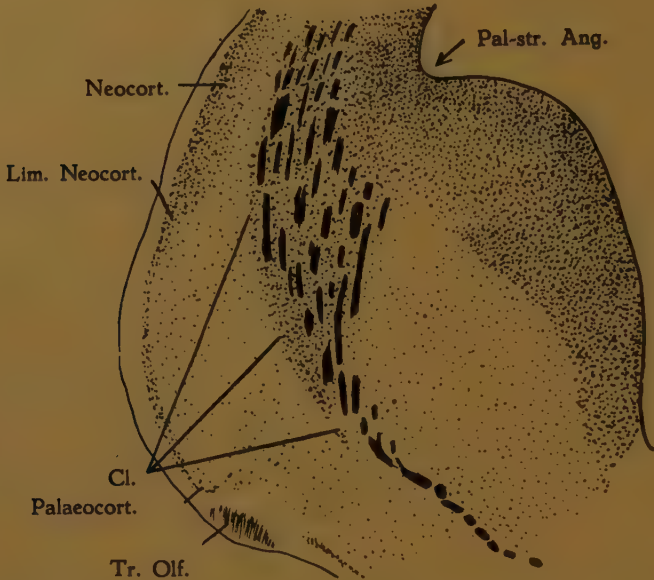


Fig. 3. Transverse section of a 36 mm. Embryo of *Sus scropha*.

of the claustrum being from the same portion of ventricular matrix which also gives rise to neocortex. The claustrum however stretches obliquely downwards and outwards from the pallio-striatal angle to the junction of the neo- and palaeocortex and does not form exactly the lower boundary of the neo-cortex. That the claustrum partly extends underneath the rhinencephalic sulcus was stated already by KAPPERS, (1908) and was confirmed by E. DE VRIES.

Whereas BRODMANN regarded the claustrum as a derivative of the sixth or innermost layer of the insular cortex cut off by the extreme capsule, LANDAU points out that:

1. The insular cortex without the claustrum shews a well developed six layered cortex.
2. Embryologically the innermost layer (the multiform layer of BRODMANN) is never connected with the claustrum. On the contrary when one examines suitable preparations, the embryonic claustrum lies further apart from the innermost insular cortex than in the adult.

He concludes that the claustrum is to be considered as an independent structure which is neither secondarily split off from the insular cortex nor from the striatum, a conclusion that I must confirm. It is a nucleus of its

own and belongs with the nucleus caudatus putamen globus pallidus and amygdala to the subpallial grey substance.

My own observations show that there is a close relation between the formation of the claustrum and that of the external capsule.



Fig. 4. Transverse section of a 36 mm. embryo of Homo.

If we would explain the development of the claustrum on neurobiotactic principles we should look for the causative stimuli in the basal region of the brain and especially in fibres running in the external capsule.

In connection with my previous studies I am struck by the great similarity between the position of the claustrum in mammals and the deeper cells of the primordium neopallii in reptiles. As soon as the two outer layers of the cortex begin to develop in ontogeny we see the beginning of claustral development in opposite direction from the ventricular matrix. I have mentioned in my previous paper that a similar relation is observed in reptilia where we find pallial cells acquiring a very close relationship with the neostriatum in the region of the primordium neopallii.

Reviewing the relations of the basal region of the forebrain to the pallium in amphibia, reptilia and mammalia, in regard to their appearance in development, we always find a close succession of subpallial structures to those of the pallium. We have seen that following on the differentiation of the tertiary olfactory cortex or archipallium, we have the appearance of the archistriatum. With the appearance of the general pallium between the archicortex and the palaeocortex, we have the first appearance of the neostriatum and as a more specialised pallium becomes evolved in mammals we

have again a submergence of its ventro-lateral edge to form the claustrum.

It seems therefore that the subpallial areas with the progress of pallial development receive an increment corresponding more or less to each newly evolved part of the pallium. What influences are at work in the determination of these developments of the ventro-lateral wall of the brain?

KAPPERS has pointed out the order of development of these parts and their relation to corresponding evolutions of the diencephalon.

So the basal forebrain bundle connects the palaeostriatum to the hypothalamus and peduncular nuclei (the future substantia nigra).

More dorsal bundles convey the neurobiotactic influences which cause the outgrowth of the neostriatum as ELLIOT SMITH first stated for birds. They also convey the fibres which run to the pallium in Reptiles above the piriform lobe and apparently lead to the differentiation of a so called primordium neopallii, and most probably contain the fibres, which influencing the so called general cortex cause it to be dragged down into the dorso-lateral part of the neostriatal ridge.

The primordium neopallii, as we have seen, has a very intimate relation to the dorso-lateral part of the anterior region of the striatum. It sinks down here from the general cortex, taking up a position in the neostriatum. This is most likely to be explained by the neurobiotactic influence of the fibres running in the ascending forebrain bundle a dorsal peduncle — the tractus thalamo-striatalis and -frontalis. So stimuli from behind cause the down-growth of the lateral pallial edge in the direction of the incoming fibres, forming the projection to which CROSBY and E. SMITH attached the name primordium neopallii.

It is my opinion that the formation of the claustrum is also caused by ascending fibres running in the forebrain peduncle — a constituent of the basal forebrain peduncle.

Besides the claustrum probably has connections with the underlying striatum.

The studies of KINNEAR WILSON make it plain that the connections of the striatum are partly endogenous connecting different parts of the striatum itself and that the chief outlet is by the old route in the ansa lenticularis and ansa peduncularis. On the other hand its connections with the cortex are slight in either direction. Similarly a stimulative effect on the outgrowth of the claustrum is not to be expected from the side of the cortex itself.

Résumé.

The claustrum can be traced ontogenetically from the ventricular matrix where this touches the striatum at the pallio-striatal angle. It extends from this point downwards and laterally beyond the lower edge of the neocortex thus reaching partly underneath the rhinencephalic cortex. The mechanism of its formation seems to be as follows: As soon as active proliferation occurs in the epithelial matrix at the pallio-striatal angle to

form the neocortex, the lowermost proliferating cells at this angle are drawn downwards towards the ascending stimuli of the fibres of the external ascending forebrain bundle. This process goes on continually and by this gradual migration the platelike claustrum is formed, the lowest cells of which are the first to develop.

There is no process of differentiation of the claustral cells in layers such as goes to form the highly characteristic layers of the neocortex. There only appears to be a gradual outpouring of cells which remain fairly equal.

I find myself in agreement with E. DE VRIES and LANDAU:

1. That the claustrum at no stage of its development belongs to the striatum.

2. That the source of its cells is the same as that of the cortex and

3. That at no time in its development the human claustrum does have relations with the cortex, but that it is an independent derivative.

DE VRIES thinks that the claustrum is a portion of the neopallium which instead of forming the superficial cortex is drawn downwards subcortically and develops further there. That is, the claustrum and cortex have a similar origin.

It is my belief that the outgrowth of the striatum, claustrum and the lamination of the cortex are independent processes, governed by the type and diversity of the fibres reaching the lateral brainwall, similarly as the formation of the hypopallial parts of the neostriatum is an inward growth of pallial matrix under the influence of ascending thalamo-striatal fibres (ELL. SMITH).

The formation of the palaeocortex is probably a process of a neurobiotactic nature brought about by the influence of stimuli running upward in the basal forebrain bundle.

The formation of the palaeocortex is probably a process of a neurobiotactic brainwall by the neurobiotactic influence of the lateral olfactory tract that runs over this surface. That the cortex of the neopallium arises by a shifting of cells to the surface although its ascending tracts come from the centre, must be due to the fact that the ascending neocortical tracts end in the superficial (not in the deeper) parts of the neopallium (layers II, III, and IV; KAPPERS).

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Mathematics. — "*Dimensionstheoretische Konsequenzen des Verhältnisses von allgemeinen Räumen und Zahlenräumen*". By Dr. K. Menger. (Communicated by Prof. L. E. J. Brouwer).

(Communicated at the meeting of March 27, 1926).

In der ersten Mitteilung über das Verhältnis von allgemeinen Räumen und Zahlenräumen ¹⁾ wurde bewiesen, dass jeder kompakte eindimensionale Raum homöomorph sei mit einer Teilmenge des R_3 , des dreidimensionalen Zahlenraumes. Der daselbst angeführte Beweis ermöglicht aber eine wesentliche Verschärfung dieser Behauptung, nämlich die Aussage: *Jeder kompakte eindimensionale metrische Raum (und insbesondere jede eindimensionale abgeschlossene Teilmenge des Würfels) ist homöomorph mit einer Menge des R_3 , zu deren sämtlichen Punkten beliebig kleine Polyeder existieren, deren Begrenzungen mit der Menge höchstens null-dimensionale Durchschnitte haben.* Und ebenso wird sich aus dem Beweis des am Ende der erwähnten Arbeit angeführten Satzes von der Einbettbarkeit aller endlichdimensionalen kompakten Räume in Zahlenräume die Verschärfung ergeben: *Jeder kompakte n -dimensionale Raum ist homöomorph mit einer Menge eines Cartesischen Raumes, auf deren sämtliche Punkte sich Polytope zusammenziehen, deren Begrenzungen mit der Menge höchstens $(n-1)$ -dimensionale Durchschnitte haben* ²⁾.

Im Folgenden soll nun der BROUWERSche Satz von der n -Dimensionalität des R_n (und damit implizit der BROUWERSche Satz von der Invarianz der Dimensionszahl) hergeleitet werden aus den zwei folgenden Annahmen:

Annahme I. Eine beschränkte abgeschlossene $(n-2)$ -dimensionale Menge des R_n ist homöomorph mit einer Menge des R_n , auf deren sämtliche Punkte sich Polytope zusammenziehen, deren Begrenzungen mit der Menge höchstens $(n-3)$ -dimensionale Durchschnitte haben.

¹⁾ These Proceedings 29, p. 476, 1926.

²⁾ An anderer Stelle (Über die Dimension von Punktmengen II, Monatshefte f. Math. u. Phys. 34, 1924, S. 160) habe ich bewiesen, dass zu jedem Punkt p einer höchstens n -dimensionalen Menge M des R_{n+1} beliebig kleine topologische Kugeln existieren, deren Begrenzungen mit der Menge M höchstens $(n-1)$ -dimensionale Durchschnitte haben, und darunter sogar topologische Kugeln von ganz besonderer Art, nämlich mit der schon von MINKOWSKI (Geometrie der Zahlen. S. 36) betrachteten Eigenschaft, dass in jeder Richtung von p aus genau ein Punkt der Begrenzung der topologischen Kugel liegt. Auf die Möglichkeit eines Beweises für die n -Dimensionalität des R_n durch die Beschränkung auf Umgebungen spezieller Art in der Definition der n -dimensionalen Mengen wird bereits in der angeführten Abhandlung über die Dimension, sowie in meinem Bericht über die Dimensionstheorie (Jahresber. d. deutschen Mathem. Vereinigung, 36, 1926) hingewiesen.

Annahme II. Eine beschränkte abgeschlossene Menge des R_n , welche homöomorph ist mit einer den R_n zerlegenden Menge (d.h. mit einer Menge, deren Komplement zum R_n nicht zusammenhängend ist), zerlegt den R^n ³⁾.

Der R_n ist sicher höchstens n -dimensional. Dass er auch nicht weniger als n -dimensional sein kann, ist bewiesen, wenn gezeigt ist, dass die Begrenzung keiner beschränkten Umgebung des R_n weniger als $(n-1)$ -dimensional ist, oder, dass die offenbar gleichbedeutende Aussage S gilt: Das Komplement einer jeden beschränkten abgeschlossenen höchstens $(n-2)$ -dimensionalen Menge zum R_n ist zusammenhängend. Diese Behauptung ist für $n=1$ trivial. Wir können die Voraussetzung S_{n-1} machen, es sei bereits bewiesen, dass das Komplement einer beschränkten abgeschlossenen höchstens $(n-3)$ -dimensionalen Menge zum R_{n-1} stets zusammenhängend ist.

Aus dieser Voraussetzung S_{n-1} und den Annahmen I und II wollen wir einen Widerspruch herleiten gegen die Annahme der Ungiltigkeit von Satz S_n , gegen die Annahme also, dass es eine beschränkte abgeschlossene $(n-2)$ -dimensionale Menge des R_n gebe, deren Komplement nicht zusammenhängend ist. Nach Annahme I wäre die betreffende Menge homöomorph mit einer Menge M des R_n , zu deren sämtlichen Punkten beliebig kleine Polytope existierten, deren Begrenzungen mit M höchstens $(n-3)$ -dimensionale Durchschnitte haben. Nach Annahme II wäre auch das Komplement von M , d.h. die Menge $R_n - M$, nicht zusammenhängend. Sei A eine Komponente von $R_n - M$, c ein Punkt der Begrenzung einer Komponente K von $R - \bar{A}$. Wir betrachten ein c enthaltendes Polytop P , dessen Begrenzung B mit M einen höchstens $(n-3)$ -dimensionalen Durchschnitt hat und das überdies so klein gewählt wird, dass $R - \bar{P}$ Punkte sowohl von A als auch von K enthält. Dann enthält auch die laut Voraussetzung S_{n-1} zusammenhängende Menge $B - B \cdot M$ Punkte sowohl von A als auch von K ⁴⁾; also wäre $A + (B - B \cdot M)$ eine zusammenhängende Teilmenge von $R_n - M$, welche A als echten Teilmengen enthält, im Widerspruch zur Komponentennatur der Menge A .

Durch diesen Widerspruch, zu dem die Annahme von der Ungiltigkeit der Behauptung S_n führt, ist Satz S unter den Annahmen I und II allgemein bewiesen.

³⁾ Auf den Beweis dieses Satzes von der Invarianz der einen Zahlenraum zerlegenden Mengen und eines wesentlich allgemeineren Satzes soll in einer folgenden Note eingegangen werden.

⁴⁾ A ist ja zu $B \cdot M$ fremd und $K \cdot B$ ist als in B offene Menge, da $B \cdot M$ in B nirgends dicht ist, nicht leer.

